

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of Rakowski

Application Serial No. 10/654,203

Filing Date: September 3, 2003

Art Unit 1793

Examiner Jesse R. Roe

Confirmation No. 5809

OXIDATION RESISTANT FERRITIC  
STAINLESS STEELS

Attorney Docket No. RL-2000

**APPEAL BRIEF – PART 1 of 2**

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Alexandria, VA 22313-1450

ATI Properties, Inc., owner of the entire right, title, and interest in the above-identified patent application (the "Subject Application"), submits this Appeal Brief in accordance with the provisions of 37 C.F.R. § 41.37 in response to: (i) the final Office Action mailed on November 23, 2009; (ii) the Advisory Action mailed on January 8, 2010; and (iii) the Notice of Appeal filed on April 22, 2010. The Commissioner is hereby authorized to charge PTO Deposit Account No. 11-1110 for any fees necessary for consideration of this brief and appeal.

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**I. REAL PARTY IN INTEREST**

The real party in interest is ATI Properties, Inc., by reason of assignment of the Subject Application and the invention from the inventor, recorded at Reel 014830, Frame 0265. ATI Properties, Inc., is a wholly-owned subsidiary of Allegheny Technologies Incorporated.

## **II. RELATED APPEALS AND INTERFERENCES**

Appellant is not aware of any other appeals or any interferences that may be related to, may directly affect or be directly affected by, or have a bearing on, the decision of the Board in the present appeal.

### **III. STATUS OF CLAIMS**

Claims 1-6, 9-11, 13, 14, 16, 18, 20-28, and 99-101 are pending in the Subject Application. Claims 7, 8, 12, 15, 17, 19, and 29-98 were previously canceled. Claims 6, 14, 23, 24, 27, and 28 currently stand withdrawn from consideration.

Claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 are currently under examination. Claims 1, 10, 11, and 99 are independent claims.

In the final Office Action issued on November 23, 2009, claims 11, 13, 16, 18, 20-22, 25, 26, and 101 stand rejected under 35 U.S.C. § 112, first paragraph, as allegedly not complying with the written description requirement. Claims 99-101 stand rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite.

Claims 1-5, 9-11, 13, 16, 18, 20-22, and 26 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over U.S. Patent No. 4,097,311 to Ishibashi et al. ("Ishibashi").

Claims 1-5, 9-11, 13, 16, 18, 20-22, 25-26, and 99-101 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer et al., "Hydrogen surface effects in ferritic stainless steels", *J. Alloys and Compounds*, 293-295 (1999), pp. 356-360 ("Szummer") in view of Japan Patent Publication No. 10-280103 to Ono et al. ("Ono").

Claims 1-5, 9-11, 13, 18, 21, 25-26, 99, and 101 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of International Patent Application Publication No. WO 99/10554 to Linden et al. ("Linden").

Claims 1-5, 9-11, 13, 18, 21, and 25-26, 99 and 101 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of Japan Patent Publication No. 06-172933 to Uematsu et al. ("Uematsu").

Claims 1-5, 9-11, 13, 16, 18, 20-22, 25-26, 99, and 101 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of Japan Patent Publication No. 09-209092 to Matsui et al. ("Matsui").

On January 22, 2010, Applicant filed a response to the November 23, 2009 final Office Action. On January 28, 2010, the Examiner issued an Advisory Action stating that Applicant's response dated January 22, 2010 failed to place the Subject Application in a condition for allowance. The January 28, 2010 Advisory Action indicated that the rejection of claim 101 under 35 U.S.C. § 112, first paragraph, was withdrawn, but that all other rejections were maintained.

On April 22, 2010, Appellant filed a notice of appeal and a request for pre-appeal brief review. The pre-appeal brief panel issued a notice of decision on May 6, 2010 indicating that the present appeal was to proceed to the Board of Patent Appeals and Interferences.

Claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 stand rejected and are the subject of the present appeal. The text of claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 is presented in the *Claims Appendix* of this *Appeal Brief*. The text of the withdrawn and cancelled claims is not presented in the *Claims Appendix*.

#### **IV. STATUS OF AMENDMENTS**

In Applicant's January 22, 2010 response to the November 23, 2009 final Office Action, claims 99 and 100 were amended to address formalities and to recite "wherein the exposed electropolished surface is uncoated." Applicant believed that these amendments did not raise new issues that would require further consideration and/or search because the Examiner presented arguments in the final Office Action regarding uncoated electropolished surfaces in connection with claim 11, which was not amended in the response. Nevertheless, the Examiner denied entry of the amendments presented in the January 22, 2010 response. Accordingly, the text of claims 99 and 100 presented in the *Claims Appendix* of this *Appeal Brief* does not reflect the amendments presented in the January 22, 2010 response.



## V. SUMMARY OF CLAIMED SUBJECT MATTER

All references herein to the "Specification" of the Subject Application refer to the paragraph numbers, page numbers, and/or figures of the specification as originally filed. References to the *Specification* do not refer to the paragraph numbers of United States Patent Application Publication No. 2005/0045250. The claims under consideration in the present appeal include four (4) independent claims, claims 1, 10, 11, and 99, which recite:

1. A method for making a ferritic stainless steel article having an oxidation resistant surface, the method comprising:
  - providing a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent; and
  - electropolishing at least one exposed surface of the ferritic stainless steel, so that, when subjected to an oxidizing atmosphere at high temperature, the exposed electropolished surface develops an electrically conductive, aluminum-rich, oxidation resistant oxide scale comprising chromium and iron and having a hematite structure differing from  $\text{Fe}_2\text{O}_3$ , alpha  $\text{Cr}_2\text{O}_3$ , and alpha  $\text{Al}_2\text{O}_3$ .
10. A method for making a ferritic stainless steel article having at least one oxidation resistant surface, the method comprising:
  - providing a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent; and
  - electropolishing at least one exposed surface of the ferritic stainless steel, so that the exposed electropolished surface develops an aluminum-rich oxide scale when heated in an oxidizing atmosphere for at least 100 hours at a temperature in the range of 750°C to 850°C, the oxide scale comprising iron and chromium and having a hematite structure,  $a_0$  in the range of 4.95 to 5.04 Å, and  $c_0$  in the range of 13.58 to 13.75 Å.

11. A method for making a ferritic stainless steel article having an uncoated electropolished oxidation resistant surface, the method comprising:  
providing a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent; and

electropolishing at least one exposed surface of the ferritic stainless steel.

99. A method for making a ferritic stainless steel article having at least one oxidation resistant surface, the method comprising:

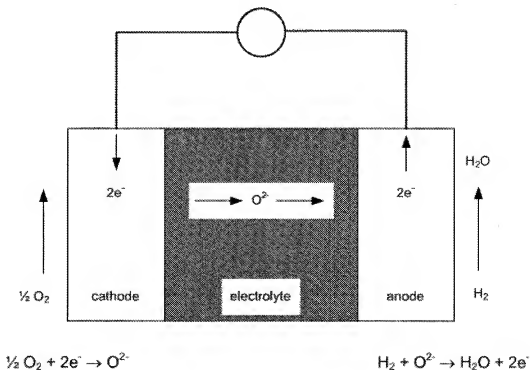
electropolishing at least one exposed surface of a ferritic stainless steel comprising 0.4 to 0.8 weight percent aluminum, 18 to 22 weight percent chromium, and 0.02 to 0.2 weight percent rare earth metals, wherein the rare earth metals are selected from the group consisting of cerium, lanthanum, praseodymium, and combinations of any thereof;

wherein the electropolishing chemically modifies the at least one exposed surface of the ferritic stainless steel so that the electropolished exposed surface develops an aluminum-rich oxide scale when heated in an oxidizing atmosphere at a temperature in the range of 750°C to 850°C, aluminum-rich the oxide scale comprising iron and chromium and having a hematite structure,  $a_0$  in the range of 4.95 to 5.04 Å, and  $c_0$  in the range of 13.58 to 13.75 Å.

Solid oxide fuel cells (SOFCs) generate electric power through electrochemical reactions. A single SOFC comprises an anode and a cathode separated by a solid oxide ceramic electrolyte, which is typically a form of stabilized zirconia, such as, for example, yttria-stabilized-zirconia (YSZ). The solid oxide electrolyte divides a SOFC into a fuel side and an oxidant side. During operation, the fuel side contains a fuel fluid, such as, for example, methane, hydrogen, petroleum-based fuels, coal gas, and the like, which are chemically capable of being oxidized. During operation, the oxidant side contains an oxidant, such as, for example, oxygen or oxygen-containing gas mixtures

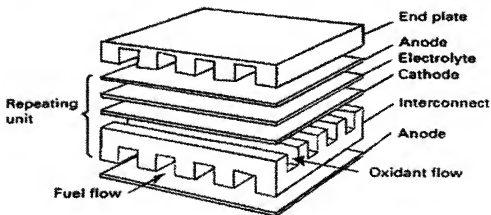
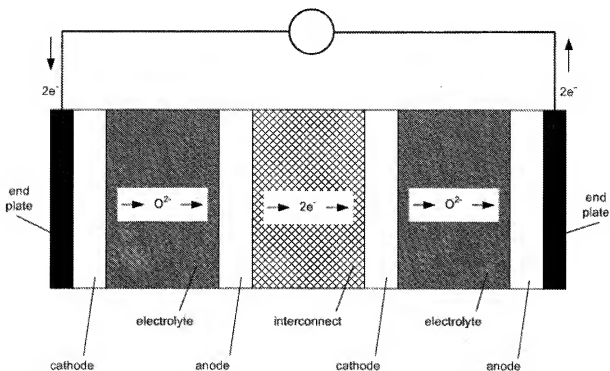
(e.g., air), which are capable of being reduced. Generally, the fuel side corresponds to the anode of a SOFC and the oxidant side corresponds to the cathode of a SOFC.

In operation, a fuel is oxidized (e.g., combusted) at the anode where it releases electrons. The electrons transport through an external circuit to the cathode. Molecular oxygen ( $O_2$ ) is reduced at the cathode by the electrons from the external circuit, forming oxide anions ( $O^{2-}$ ). The solid oxide electrolyte is permeable to the oxide anions, which transport through the electrolyte from the cathode to the anode. The combined ionic flow through the electrolyte and the electrical flow through the external circuit completes the electrochemical circuit. This process is illustrated below with molecular hydrogen ( $H_2$ ) as the fuel, for example.



Useful power is extracted from a SOFC by using the electrons transporting through the external circuit to do work. However, the amount of energy available from a single SOFC is limited. Hence, planar SOFC stacks have been developed. Planar SOFCs comprise two or more single SOFCs stacked together in series. The individual SOFCs comprising a planar SOFC stack are separated by structures called

interconnects. Interconnects function to collect and transport the electrons generated by the electrochemical reactions in the individual fuel cells. Interconnects also function as a physical separator between the fuel streams and the oxidant streams associated with the anodes and cathodes, respectively, of adjacent SOFCs in a stack. A planar SOFC stack comprising two SOFCs in series is illustrated below.



The material used to form SOFC interconnects must be electrically conductive to complete the electrochemical circuit. In addition, because interconnects are positioned adjacent to anodes and cathodes in SOFCs, the material used to form interconnects must be oxidation resistant, thermally stable, and mechanically stable.

SOFCs operate over a wide range of temperatures. For example, at start-up, a SOFC may be around room temperature. During operation, the temperature of a SOFC may reach temperatures of 1000°C or more. In addition, temperature fluctuations during operation may expose the materials forming SOFCs to substantial thermal cycling. As a result, it is important that the material used to form interconnects have thermal expansion properties, such as, for example, a coefficient of thermal expansion (CTE), substantially similar to the materials used to form other components of the SOFC, such as anodes, cathodes, and electrolytes, which contact or are in very close proximity to the interconnect.

As mentioned above, SOFC electrolytes are typically formed of solid oxide ceramics, such as YSZ or other stabilized zirconia. SOFC anodes and cathodes are also commonly formed from ceramic or ceramic-metal composite (cermet) materials. Accordingly, SOFC interconnects have previously been fabricated from ceramic materials that are electrically conductive at SOFC operating temperatures, for example, lanthanum chromite ( $\text{LaCrO}_3$ ) doped with calcium oxide ( $\text{CaO}$ ) or strontium oxide ( $\text{SrO}$ ). However, doped ceramic materials are brittle, expensive, and poor electrical conductors, particularly when compared to metals and metal alloys.

Fabricating SOFC interconnects from stainless steels provides certain advantages because steels have relatively good electrical conductivity and are less brittle than ceramics. However, in interconnect applications, stainless steels may exhibit certain undesirable properties such as relatively high levels of oxidation, thermal expansion, and creep. Nevertheless, the present inventor discovered that electropolishing a ferritic stainless steel comprising certain compositional features will result in a material that functions exceptionally in SOFC interconnect applications due to

a novel and non-obvious oxide scale that develops on the material when subjected to an oxidizing atmosphere at high temperatures.

The present inventor discovered that a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, 16 to less than 30 weight percent chromium, and at least one rare earth metal, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent, will develop an electrically conductive and oxidation resistant oxide scale on electropolished surfaces when subjected to an oxidizing atmosphere at high temperatures, such as, for example, the atmospheres characteristic of SOFCs.

*Specification*, ¶¶ [0013], [0015], [0050]-[0051]. Such oxidizing atmospheres may include, for example, temperatures in the range of 750°C to 850°C. *Id.* at ¶¶ [0005] and [0014]-[0015]. The internal components of SOFCs are often exposed to such oxidizing atmospheres for at least 100 hours at temperature during operation. *Id.* The distinctive oxide scale is aluminum-rich and comprises aluminum, chromium, and iron. *Id.* at ¶¶ [0067]-[0068]. Further, the distinctive oxide scale has a hematite structure differing from  $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-Cr}_2\text{O}_3$ , and  $\alpha\text{-Al}_2\text{O}_3$ . *Id.*

As is known in the art, the term "hematite structure" generally refers to trigonal-hexagonal scalenohedral crystal structures of minerals and ceramic materials having the general chemical formula:  $\text{X}_1^{[3+]} \text{Y}_1^{[3+]} \text{O}_3^{[2-]}$ , wherein the "X" and "Y" designate electropositive elements having a three electron deficient valance. The hematite crystal structure includes single metal oxides and mixed metal oxides. Iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ), chromium (III) oxide ( $\text{Cr}_2\text{O}_3$ ), and aluminum (III) oxide ( $\text{Al}_2\text{O}_3$ ) are three single metal oxides having hematite structures that structurally differ from each other in terms of the distances between the atoms in the crystal lattice. The inter-atomic distances between atoms in a crystal lattice are generally reported in the art as the lattice parameters  $a_0$  and  $c_0$  for a lattice unit cell, which are generally measured using diffractometry. See *Specification*, ¶¶ [0066]-[0068].

The distinctive oxide scale characteristic of the methods recited in the claims of the Subject Application is a single-phase composition having a hematite structure (*id.* at ¶ [0067]) and, therefore, may be described by the formula  $(\text{Al,Cr,Fe})_2\text{O}_3$ .

The lattice parameters of the oxide scale differ from the lattice parameters of  $\text{Fe}_2\text{O}_3$ , alpha  $\text{Cr}_2\text{O}_3$ , and alpha  $\text{Al}_2\text{O}_3$ . *Id.* For example, the oxide scale may be characterized by lattice parameters  $a_o$  in the range of 4.95 Å to 5.04 Å and  $c_o$  in the range of 13.58 Å to 13.75 Å. *Id.* By way of comparison, the lattice parameters of  $\text{Fe}_2\text{O}_3$ , alpha  $\text{Cr}_2\text{O}_3$ , and alpha  $\text{Al}_2\text{O}_3$  are provided in the table below, in addition to the nominal lattice parameters of the distinctive aluminum-rich oxide scale characteristic of the methods recited in the claims of the Subject Application. *Id.* at ¶¶ [0067]-[0068] and Table 5, p.33.

	$a_o$ (Å)	$c_o$ (Å)
$\text{Al}_2\text{O}_3$	4.758	12.991
$\text{Cr}_2\text{O}_3$	4.954	13.584
$(\text{Al,Cr,Fe})_2\text{O}_3$	4.98	13.57
$\text{Fe}_2\text{O}_3$	5.356	13.7489

Accordingly, the lattice parameters of the distinctive aluminum-rich oxide scale are significantly different than the lattice parameters of  $\text{Al}_2\text{O}_3$  notwithstanding that the novel scale is aluminum-rich. *Id.* at ¶ [0068]. The aluminum-rich composition of the distinctive scale significantly improves the high temperature oxidation resistance of the particular electropolished ferritic stainless steels because aluminum-rich mixed metal oxide is non-volatile, adherent, and has a relatively slow growth rate. In contrast, chromium-rich oxides are relatively volatile and will evaporate from the surfaces of ferritic stainless steels in the presence of high temperature air and water vapor, which are commonly present in operating SOFCs. *Id.* at ¶ [0064]. Chromium-rich oxides also form more quickly than aluminum-rich oxides, which can result in migration and depletion of chromium from the underlying alloy matrix, thereby accelerating corrosion. Likewise, iron-rich oxides form more quickly than aluminum-rich oxides. Iron-rich oxides are also less adherent than aluminum-rich oxides and often spall from the underlying alloy, thereby exposing non-oxidized alloy to further corrosion.

However, the levels of iron and chromium in the distinctive aluminum-rich oxide scale are sufficient to make the scale more electrically conductive than  $\text{Al}_2\text{O}_3$ .

The increased conductivity and the decreased thickness of the distinctive aluminum-rich oxide scale result in a slower rate of increase for the area specific resistance (ASR) of ferritic stainless steel components during exposure to high temperature oxidizing environments, such as in SOFC operation. *Id.* at ¶ [0064].

The distinctive aluminum-rich oxide scale characteristic of the methods recited in the claims of the Subject Application forms because of an electrochemical modification of the surface of the ferritic stainless steel that occurs during the electropolishing step. *See id.*, *Example 1*, at ¶¶ [0052]-[0056] and *Example 2*, at ¶¶ [0059]-[0063]. Therefore, the electrochemically modified surfaces are significantly more oxidation resistant at high temperatures than non-electropolished ferritic stainless steels or ferritic stainless steels having different concentrations of aluminum, chromium, and rare earth metals. In addition, the electropolished oxidation resistant surface is uncoated. *See, e.g., id.* (describing the electropolishing of ferritic stainless steel samples that do not have any coating applied to the surfaces of the articles, thus forming uncoated electropolished oxidation resistant surfaces).

Further, the concentrations of aluminum, chromium, and rare earth metals recited in claims 1, 10, 11, and 99 are critical to the development of the distinctive aluminum-rich oxide scale on the electropolished surfaces of ferritic stainless steels, and to the resulting significant improvement in high temperature oxidation resistance. *See id.*, *Example 4*, at ¶¶ [0069]-[0073] (describing the oxidation resistance properties of electropolished ferritic stainless steels having varying concentrations of aluminum, chromium, and rare earth metals).

In light of the high temperature oxidation resistance of ferritic stainless steels processed according to the methods recited in the claims of the Subject Application, such steels may be advantageously applied as interconnects for fuel cells, including SOFCs. Moreover, examples of additional articles of manufacture that may be advantageously constructed to include ferritic stainless steels processed according to the recited methods include apparatuses subjected to high temperature oxidizing environments, such as, for example, high-temperature manufacturing equipment, high-



temperature handling equipment, calcining equipment, glass making equipment, glass handling equipment, and heat exchanger components. In addition, ferritic stainless steel articles such as, for example, plate, sheet, strip, foil, and bar that are intended for fabrication into articles of manufacture, may be processed using the recited methods. Id. at ¶ [0074].

**VI. GROUND S OF REJECTION TO BE REVIEWED ON APPEAL**

(1) The rejection of claims 11, 13, 16, 18, 20-22, 25, and 26 under 35 U.S.C. § 112, first paragraph, as allegedly failing to comply with the written description requirement.

(2) The rejection of claims 99-101 under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite.

(3) The rejection of claims 1-5, 9-11, 13, 16, 18, 20-22, and 26 under 35 U.S.C. § 103(a) as allegedly being unpatentable over Ishibashi.

(4) The rejection of claims 1-5, 9-11, 13, 16, 18, 20-22, 25-26, and 99-101 under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of Ono.

(5) The rejection of claims 1-5, 9-11, 13, 18, 21, 25-26, 99, and 101 under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of Linden.

(6) The rejection of claims 1-5, 9-11, 13, 18, 21, and 25-26, 99 and 101 under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of Uematsu.

(7) The rejection of claims 1-5, 9-11, 13, 16, 18, 20-22, 25-26, 99, and 101 under 35 U.S.C. § 103(a) as allegedly being unpatentable over Szummer in view of Matsui.

## VII. ARGUMENT

A. Claims 11, 13, 16, 18, 20-22, 25, and 26 comply with the written description requirement under 35 U.S.C. § 112, first paragraph.

1. The standards for compliance with the written description requirement.

The written description requirement under 35 U.S.C. § 112, first paragraph, requires that the specification convey with reasonable clarity to those skilled in the art that the applicant was in possession of the invention as claimed. *Vas-Cath, Inc. v. Mahurkar*, 935 F.2d 1555, 1563 (Fed. Cir. 1991); MPEP § 2163. "If a skilled artisan would have understood the inventor to be in possession of the claimed invention at the time of filing, even if every nuance of the claims is not explicitly described in the specification, then the adequate description requirement is met." *Id.*

Under the written description inquiry, "a claim will not be invalidated on § 112 grounds simply because embodiments of the patent specification do not contain examples explicitly covering the full scope of the claim language." *LizardTech, Inc. v. Earth Resource Mapping, Inc.*, 424 F.3d 1336, 1344-45 (Fed. Cir. 2005). Rather, because the patent specification is written for a person having skill in the art, it is unnecessary to spell out every detail of the invention. The specification need only include enough information to indicate to a person having skill in the art that the inventor possessed the invention as claimed. *Id.*

Regarding the written description requirement, the MPEP states that "[w]henver the issue arises, the fundamental factual inquiry is whether the specification conveys with reasonable clarity to those skilled in the art that, as of the filing date sought, applicant was in possession of the invention as now claimed." MPEP § 2163.02 (case law citations omitted). Further, the MPEP states that "[t]he subject matter of the claim need not be described literally (*i.e.*, using the same terms or *in haec verba*) in order for the disclosure to satisfy the description requirement." MPEP § 2163.02. Thus, compliance with the written description requirement does not require literal support

using the same terms in the specification and in the claims, provided that a person skilled in the art could reasonably conclude that the inventor had possession of the claimed invention. MPEP § 2163.I.

**2. The recitation "uncoated" in claim 11 is properly supported by the specification.**

The Examiner asserts that claims 11, 13, 16, 18, 20-22, 25, and 26 lack written description support because the specification allegedly does not describe a ferritic stainless steel article having an uncoated electropolished surface as recited in claim 11. Appellant respectfully disagrees. Appellant respectfully submits that the Examiner is applying an improper *in haec verba* requirement by stating that the Specification does not recite "without a coating" or "uncoated" and, therefore, arguing that this feature does not have a basis in the original disclosure.

Here, a person skilled in the art would have understood the inventor to have been in possession of a method for making a ferritic stainless steel article having an uncoated electropolished oxidation resistant surface at least based on Examples 1 and 2 in the Specification, which describe the making of a ferritic stainless steel article having an uncoated, electropolished, and oxidation resistant surface. *See Specification*, ¶¶ [0052]-[0058] (describing the casting, hot reducing, cold rolling, annealing, grinding, electropolishing, and oxidation testing of a ferritic stainless steel article that is, in fact, not coated).

The Examiner cites to MPEP § 2173.05(i) as allegedly supporting the argument that the Specification must literally recite "without a coating" or "uncoated" in order to support claim 11 and its dependent claims. However, this section of the MPEP states "that a lack of literal basis in the specification for a negative limitation may not be sufficient to establish a *prima facie* case for lack of descriptive support." (Emphasis added).

The MPEP further states that "[b]y disclosing in a patent application a device that inherently performs a function or has a property, operates according to a theory or has an advantage, a patent application necessarily discloses that function, theory or advantage, even though it says nothing explicit concerning it." "The application may later be amended to recite the function, theory or advantage without introducing prohibited new matter." MPEP § 2163.07(a) (emphases added, case law citations omitted).

The ferritic stainless steel articles made and tested in Examples 1 and 2 in the Specification are inherently uncoated. Nowhere does Example 1 or Example 2 describe coating the ferritic stainless steel articles. In fact, Example 1 in the Specification describes the following (§ [0052]):

A coil of AL 453™ alloy was provided by the conventional process of casting the alloy to a slab or ingot, hot reducing to a band, cold rolling to finished gauge with intermediate stress relieving anneals, and a final anneal in hydrogen. Several 1" x 2" test coupons were prepared from the coil and processed by three different surface treatments. Each coupon had an initial thickness of 0.075" and a standard 2BA finish, and was degreased and had finished edges. This surface finish is generally referred to herein as a 'mill' surface, and samples including that surface are referred to herein as 'mill' samples. Several mill samples were further processed by grinding using 120 grit SiC paper to remove nominally 0.005" per side. Samples prepared in this way are referred to herein as 'ground' samples. Several of the ground samples were electropolished in an electropolishing solution including, by volume, 25% sulfuric acid - 47% phosphoric acid - 28% glycolic acid for 20 minutes (samples flipped every 5 minutes) at 1 amp/inch<sup>2</sup> at approximately 170°F (about 77°C) to provide several 'electropolished' samples.

A person skilled in the art would readily and unambiguously recognize that the "electropolished" samples prepared in Example 1 were, in fact, uncoated. The ferritic stainless steel was cast, hot reduced, cold rolled, annealed, ground, and electropolished. Clearly, the "electropolished" samples were never coated in Example 1. Moreover, as a factual matter, any coating present on the surfaces of the articles would be removed by the grinding, which was performed immediately before the electropolishing.

Example 1 further describes that the three surface types (*i.e.*, mill, ground, and electropolished) were characterized using electron microscopy both before exposure to an oxidizing atmosphere and after exposure to an oxidizing atmosphere. *Specification*, ¶¶ [0053]-[0058]. As described in the *Specification*, "the rate of oxidation of the electropolished samples was several orders of magnitude lower than that of the mechanically finished mill and ground surfaces". *Id.* at ¶ [0056]. Thus, the specification clearly supports an "uncoated electropolished oxidation resistant surface", as recited in claim 11.

Likewise, Example 2 describes ferritic stainless steel articles having uncoated electropolished oxidation resistant surfaces. *Id.* at ¶¶ [0059]-[0063] (*see* Table 4, p.28, describing electropolished articles that had their surfaces ground before the electropolishing operation to remove 0.002 inches (nominal) from the surfaces).

Thus, according to at least the case law cited in MPEP § 2163.07(a), a method for making a ferritic stainless steel article having an uncoated electropolished oxidation resistant surface is fully supported by the *Specification*, regardless of whether the *Specification* explicitly states "uncoated". Because an article having an uncoated electropolished oxidation resistant surface was described, at least implicitly, in the *Specification* in Examples 1 and 2, the written description requirement is satisfied. MPEP § 2163.07(a) and § 2173.05(i) (case law citations omitted).

The Examiner further argues that the *Specification* does not provide support for an uncoated electropolished surface because the ferritic stainless steel recited in the present claims would be coated by an oxide scale. In particular, the Examiner refers to paragraphs [0053] and [0055] of the *Specification*, which respectively describe the native oxide scale of electropolished articles before exposure to high temperature oxidizing conditions and the distinctive aluminum-rich oxide scale after exposure. However, these oxide scales chemically develop on the surfaces of ferritic stainless steels. These oxide scales are not coatings, as the term is understood in the art.

Coatings and scales are physically different and distinct. A coating is a layer of a substance that is physically applied onto a substrate. In contrast, a scale is a layer that chemically develops on the surface and in the near-surface region of a material as a result of spontaneous chemical reactions with the surrounding environment. A scale is not physically applied onto the surface of a substrate like a coating. Rather, a scale is produced as the chemical elements that constitute a material chemically react at the material's surface with species such as oxygen in the surrounding environment. In this manner, the surface and near-surface regions of the material chemically transform into a scale layer under certain conditions. As such, a scale is physically and chemically different than and distinct from a coating.

By way of Example, Ishibashi<sup>1</sup> describes applying a coating layer to a substrate. The application of a discrete coating layer prevents the underlying substrate from chemically reacting with oxygen in the surrounding atmosphere to form an oxide scale. Indeed, the Specification does not recite the term "coated" or related terms because the electropolished surfaces of the ferritic stainless steel are inherently uncoated so that the alloy may react with oxygen in the surrounding atmosphere under high temperature oxidizing conditions to form the distinctive aluminum-rich oxide scale.

In the Advisory Action issued January 28, 2010, the Examiner states that "Applicant does not have support for the ferritic stainless steel being "uncoated" since nowhere in the Specification refers to the ferritic stainless steel as being 'without a coating' or 'uncoated'." *Advisory Action*, p.2. Accordingly, Appellant respectfully maintains that the Examiner is applying an improper *in haec verba* requirement. The Specification does not literally recite "uncoated" or the like. But, compliance with the written description requirement does not require literal support using the same terms in the Specification and in the claims, provided that a person skilled in the art could reasonably conclude that the inventor had possession of the claimed invention. MPEP § 2163(I).

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<sup>1</sup> See the discussion of Ishibashi, *infra*, Section C.2.

Here, a person skilled in the art would have understood the inventor to have been in possession of a method for making a ferritic stainless steel article having an uncoated electropolished oxidation resistant surface at least based on Examples 1 and 2 in the specification, which describe electropolishing an uncoated ferritic stainless steel. Subsequent oxidation testing demonstrated that the uncoated electropolished article developed the distinctive oxide scale recited in the claims of the Subject Application. The article was, in fact, never coated and, therefore, it is an uncoated article. The fact that the surface of the ferritic stainless steel article develops a particular oxide scale under certain conditions does not make the article "coated". This is because a physically applied coating layer and a chemically developed scale layer are different and distinct.

Thus, Appellant respectfully submits that claims 11, 13, 16, 18, 20-22, and 25-26 comply with the written description requirement and, therefore, Appellant respectfully requests reversal of the rejection under 35 U.S.C. § 112, first paragraph.

**B. Claims 99-101 are not indefinite under 35 U.S.C. § 112, second paragraph.**

**1. The standards for compliance with the requirement for definiteness.**

The essential inquiry pertaining to the requirement for definiteness is whether the claims set out and circumscribe a particular subject matter with a reasonable degree of clarity and particularity. MPEP § 2173.02. Definiteness of claim language must be analyzed, not in a vacuum, but in light of:

- (A) The content of the particular application disclosure;
- (B) The teachings of the prior art; and
- (C) The claim interpretation that would be given by one possessing the ordinary level of skill in the pertinent art at the time the invention was made.

*Id.*



In reviewing a claim for compliance with 35 U.S.C. § 112, second paragraph, the Examiner must consider the claim as a whole to determine whether the claim apprises one of ordinary skill in the art of its scope and, therefore, serves the notice function required by 35 U.S.C. § 112, second paragraph, by providing clear warning to others as to what constitutes infringement of the patent. *Id.* Accordingly, a claim term that is not used or defined in the specification is not indefinite if the meaning of the claim term is discernible. *Id.*

## **2. Claims 99-101 are not indefinite.**

The Examiner asserts that claims 99-101 are indefinite because it is allegedly unclear if aluminum is included in the oxide scale recited in claim 99 or if aluminum is lacking from the oxide scale recited in claim 99. Claim 99 originally recited, in part (emphases added):

wherein the electropolishing chemically modifies the at least one exposed surface of the ferritic stainless steel so that the electropolished exposed surface develops an aluminum-rich oxide scale when heated in an oxidizing atmosphere at a temperature in the range of 750°C to 850°C, aluminum-rich the oxide scale comprising iron and chromium and having a hematite structure,  $a_0$  in the range of 4.95 to 5.04 Å, and  $c_0$  in the range of 13.58 to 13.75 Å.

Appellant notes that this language contains a typographical error, namely the recitation of "aluminum-rich the oxide scale comprising" should read "the aluminum-rich oxide scale comprising". Appellant respectfully submits that the Examiner's alleged indefiniteness issue is due to this typographical error. In the Response to final Office Action dated January 22, 2010, Applicant amended claim 99 to correct this typographical error; however, the Examiner denied entry of the amendment. Nevertheless, Appellant respectfully submits that the Specification clearly describes the recited oxide scale as including chromium, iron, and aluminum.

Claims 1, 10, and 99 each include the feature wherein, under certain conditions, an electropolished surface develops an aluminum-rich oxide scale comprising chromium and iron and having a hematite structure. As described in detail

in the Specification, the distinctive oxide scale recited in the claims includes aluminum, chromium, and iron.

For example, paragraph [0058] of the Specification describes scanning auger microscopy analysis of the oxide scales that formed on the uncoated and exposed surfaces of samples of an electropolished ferritic stainless steel heated at 750°C and 850°C. This analysis "revealed that the oxide scale is of a single phase and contains significant concentrations of aluminum, iron, and chromium...." *Specification*, ¶ [0058]. Further, "it appeared that electropolishing promotes the formation of [the] aluminum-rich oxide scale...." *Id.*

In addition, paragraph [0064] of the Specification states that "structural characterization of the thin aluminum-rich oxides formed on electropolished [ferritic stainless steel] alloy at high temperatures...confirmed that the oxides include a significant level of iron and chromium, along with aluminum...." *Id.* at [0064]. The distinctive aluminum-rich oxide scale that formed on the electropolished ferritic stainless steel was shown to have a chemical composition and a crystal structure that are different than the oxide scale that formed on non-electropolished samples of an identical ferritic stainless steel. *Id.* at ¶¶ [0065]-[0068].

Clearly, the distinctive aluminum-rich oxide scale described in the Specification and recited in the claims includes aluminum. Therefore, Appellant respectfully requests reversal of the rejection of claims 99-101 under 35 U.S.C. § 112, second paragraph.

**C. Claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 are patentable under 35 U.S.C. § 103(a).**

**1. The standards for analyzing obviousness or nonobviousness under 35 U.S.C. § 103(a).**

Obviousness under 35 U.S.C. § 103(a) is a question of law based on at least three underlying findings of fact:

- (1) The scope and content of the prior art;
- (2) The differences between the claimed invention and the prior art; and
- (3) The level of ordinary skill in the pertinent art.

Based on these facts, the legal conclusion of whether a claim, as a whole, is obvious or non-obvious is made based on a preponderance of the evidence standard. See *Graham v. John Deere Co.*, 383 U.S. 1, 17-18 (1966); *KSR International Co. v. Teleflex Inc.*, 550 U.S. 398 (2007); *In re Oetiker*, 977 F.2d 1443 (Fed. Cir. 1992).

To this end, the Manual of Patent Examining Procedure (MPEP) provides that the contents of a § 103(a) rejection set forth in an Office Action should include:

- (1) the relevant teachings of the prior art relied upon, preferably with reference to the relevant column or page number(s) and line number(s) where appropriate;
- (2) the difference or differences in the claim over the applied reference(s);
- (3) the proposed modification of the applied reference(s) necessary to arrive at the claimed subject matter; and
- (4) an explanation as to why the claimed invention would have been obvious to one of ordinary skill in the art at the time the claimed invention was made.

MPEP § 706.02(j) (Eighth Edition, Revision 7, July 2008).

As part of the determination of the scope and content of the prior art, prior art references must be considered in their entirety, *i.e.*, as a whole, including portions that would lead away from the claimed invention. MPEP § 2141.02.VI (case law

citations omitted). As part of the determination of the differences between the claims and the prior art, all of the words and features recited in the claims must be considered in judging the patentability of the claim against the prior art. MPEP § 2143.03 (case law citations omitted). Indeed, in determining the differences between the prior art and the claims, the question under § 103(a) is whether the claimed invention as a whole would have been obvious. MPEP § 2141.02.I (case law citations omitted). It is the invention as a whole, and not some part of it, which is evaluated for obviousness under § 103. MPEP § 2141.02.V (case law citations omitted).

Accordingly, a determination regarding the obviousness or non-obviousness of the claims in a patent application involves a direct comparison of the subject matter of the claims, as a whole, to the teachings of the cited references, as a whole. A *prima facie* case of obviousness requires that the claims would have been obvious to a person skilled in the art at the time of the invention despite the differences between the claims and the teachings of the cited references. Thus, rejections on obviousness grounds cannot be sustained with mere conclusory statements or unsupported assertions. The Examiner must clearly communicate logical reasoning with rational underpinnings based on a preponderance of factual evidence to support the legal conclusion of obviousness. See MPEP § 2141; *KSR*, 550 U.S. at 418; *Oetiker*, 977 F.2d at 1446.

Appellant respectfully submits that the Examiner has failed to properly establish a *prima facie* case of obviousness under 35 U.S.C. § 103(a) and the controlling case law. In the present matter, there are very significant differences and substantial distinctions between the methods recited in the claims of the Subject Application and the subject matter disclosed in the cited references. These differences and distinctions create a very large gap between the prior art and the claimed invention that is "so great as to render the [present claims] nonobvious to one reasonably skilled in the art." MPEP 2141.III (*quoting Dann v. Johnston*, 425 U.S. 219, 230 (1976)).

**2. Claims 1-5, 9-11, 13, 16, 18, 20-22, and 26 would not have been obvious over Ishibashi.**

The Examiner asserts that claims 1-5, 9-11, 13, 16, 18, 20-22, and 26 would have been obvious over Ishibashi. Appellant respectfully disagrees for at least the following reasons.

**i. The scope and content of the prior art – the teachings of Ishibashi.**

Ishibashi describes a method for preparing a surface of an alloy component in a solar collector so that the surface advantageously absorbs solar radiation. *Ishibashi*, abstract. The method described in Ishibashi includes processing an alloy substrate so that it has a "mirror-like surface of [a] predetermined roughness", and then tightly adhering a coating of a predetermined metal oxide to the mirror-like surface. *Id.* at c.2, ll.39-48. The metal oxide is selected so that, when applied as a coating to the mirror-like surface, it has the effect of selectively absorbing solar radiation and preventing reflection of the solar radiation from the surface. *Id.*

The techniques described in Ishibashi that are used to apply the metal oxide coating onto the prepared mirror-like surface of the substrate include:

- (1) Methods for manufacturing metal oxide by the wet and dry chemical treatments.
- 30 (2) Chemical treating method for manufacturing metal oxide of the stainless steel after the stainless steel having the predetermined metal composition is tightly adhered on the substrate having the mirror-like surface other than said stainless steel.
- 35 (3) Methods for manufacturing metal oxide of the stainless steel by means of the vacuum evaporation method, the sputtering method and the arc discharging method after the stainless steel having the predetermined metal composition is tightly adhered on the substrate having the mirror-like surface other than said stainless steel.
- 40 (4) Methods for manufacturing metal oxide of the stainless steel by adhering simultaneously oxidizing the stainless steel having the predetermined metal composition on the substrate having the mirror-like surface
- 45 other than stainless steel.

*Ishibashi*, c.4, ll.26-45. *Ishibashi* explains that the oxide film applied onto the mirror-like surface has a thickness in the range of 500-2000 Angstroms. *Id.* at c.10, ll.29-38. Thus, the processed surface of the substrate in *Ishibashi* is not left exposed, but instead is actively coated with a relatively thick layer of a metal oxide material having certain spectral properties facilitating absorption of solar radiation by the coated surface.

The only reference to electropolishing in *Ishibashi* is in connection with the conventional reduction of surface roughness of a stainless steel substrate. See *Ishibashi*, c.7, ll.34-50, reproduced below.

One of the effects of the present invention is to improve the selective absorption property of the selective absorption surface of the solar collector by finishing the surface of the stainless steel substrate with the roughness of Ra less than 0.07 or Rz less than 0.2 by the mechanical polishing, the chemical abrasion and the electrolytic polishing, removing the many disadvantages 40 coming from unhomogeneous of the metal plate surface. One of the examples showing the efficiency of the selective absorption surface of the solar collector having the appropriate roughness was shown in FIG. 4. In the example, the stainless steel (304 (AISI) 683/XIII 11 45 (ISO)) was treated by a liquid honing method using glass powders of a particle size of 20 – 100 µm to form a clean surface having the surface roughness of Ra 0,2 µm or Rz 1.0 µm and then oxidized said surface according to the acidic oxidation method of the item (3a). 50

However, there is no disclosure in *Ishibashi* related to electrochemical modification of ferritic stainless steels.

ii. **Ishibashi does not teach or suggest the formation of an aluminum-rich oxide scale comprising aluminum, chromium, and iron, and having a hematite crystal structure, as recited in independent claims 1 and 10.**

Claims 1 and 10 recite that the electropolishing causes the development of an oxidation resistant, aluminum-rich oxide scale comprising chromium and iron and having a hematite structure differing from  $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-Cr}_2\text{O}_3$ , and  $\alpha\text{-Al}_2\text{O}_3$ , such as

a scale having the lattice parameters  $a_0$  in the range of 4.95 to 5.04 Å, and  $c_0$  in the range of 13.58 to 13.75 Å. The Examiner asserts that the aluminum-rich oxide scale feature recited in claims 1 and 10 is taught by the disclosure in Ishibashi at column 5, lines 14-19, which discloses the following:

Said metal oxide coming from the stainless steel consists of those having the chemical formula of  $\text{FeO}$  <sup>15</sup>  
 $(\text{FeCr})_2\text{O}_3$  in the ferritic stainless steel and  $(\text{Fe, Ni})\text{O}$   
 $(\text{Fe,Cr})_2\text{O}_3$  in the austenitic stainless steel, the both  
metal oxides being the spinel structure having the lattice  
defect.

However, these metal oxides do not include aluminum at all, let alone being aluminum-rich, as recited in claims 1 and 10. Further, Ishibashi discloses that these metal oxides have a spinel crystal structure, not a hematite crystal structure, as recited in claims 1 and 10.

A spinel crystal structure has the general formula:  $A_1^{[2+]}B_2^{[3+]}O_4^{[2-]}$ . The spinel oxide disclosed in Ishibashi satisfies this formula, wherein  $A = \text{Fe}^{2+}$  and  $B = (\text{FeCr})^{3+}$ . In contrast, a hematite crystal structure has the general formula:  $X_1^{[3+]}Y_1^{[3+]}O_3^{[2-]}$ . The aluminum-rich oxide scale recited in claims 1 and 10 satisfies this formula, wherein X and Y are independently selected from  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$ .

Accordingly, the oxide scale recited in claims 1 and 10 is compositionally and structurally different than and distinct from the oxides disclosed in Ishibashi. There is no disclosure presented in Ishibashi that teaches or suggests aluminum-rich oxides or hematite crystal structures, as recited in claims 1 and 10.

iii. **The aluminum-rich oxide scale recited in independent claims 1 and 10 would not have been inherently expected from the disclosure presented in Ishibashi.**

As described in the Specification, the present inventor discovered that an electrically conductive, slow growing, oxidation resistant, and aluminum-rich oxide scale

comprising aluminum, chromium, and iron, and having a particular hematite structure, will develop on an electropolished surface of certain ferritic stainless steels when subjected to a high temperature oxidizing atmosphere, provided that the ferritic stainless steel contains certain critical levels of aluminum, rare earth metal(s), and chromium. *Specification*, ¶¶ [0045] and [0052]-[0073]. The distinctive scale decreases the oxidation rate of the surface of the steel by several orders of magnitude relative to identical steel that has not been electropolished (*i.e.*, non-electropolished). There is nothing described in Ishibashi that would have taught or suggested these features.

Nevertheless, the Examiner asserts that Ishibashi discloses processing the same composition by the same process and, therefore, the Examiner concludes that the recited composition, crystal structure, and lattice parameters of the scale would be expected, citing to MPEP § 2112.01.I. Appellant respectfully submits that this is incorrect. This section of the MPEP describes case law that stands for the proposition that objects having the same composition and the same structure exhibit the same properties. See MPEP § 2112.01.II, which provides (emphases added):

'Products of identical chemical composition can not have mutually exclusive properties.' A chemical composition and its properties are inseparable. Therefore, if the prior art teaches the identical chemical structure, the properties applicant discloses and/or claims are necessarily present. *In re Spada*, 911 F.2d 705, 709, 15 USPQ2d 1655, 1658 (Fed. Cir. 1990) (Applicant argued that the claimed composition was a pressure sensitive adhesive containing a tacky polymer while the product of the reference was hard and abrasion resistant. 'The Board correctly found that the virtual identity of monomers and procedures sufficed to support a prima facie case of unpatentability of Spada's polymer latexes for lack of novelty.').

In other words, only the same (*i.e.*, identical) compositions necessarily have the same (*i.e.*, identical) properties. In contrast, a broad, undifferentiated range of compositions disclosed in the prior art would not be expected to inherently possess the particular structure and properties exhibited by a specific composition, especially where the structure and properties are not even suggested in the prior art.



The Examiner is apparently attempting to remedy the deficiencies in Ishibashi by relying on an inherency argument. However, as set forth in MPEP § 2141.02.V, an obviousness rejection cannot be based on a theory of inherency. Rather, in order to rely on some allegedly inherent feature of the prior art when establishing an obviousness rejection, the allegedly inherent feature must have been taught or suggested in the prior art at the time that the claimed invention was made. *In re Rijckaert*, 9 F.3d 1531 (Fed. Cir. 1993).

In the case *In re Rijckaert*, the examiner based an obviousness rejection on a combination of prior art references that failed to teach or suggest certain features recited in the rejected claims. 9 F.3d 1531. The examiner argued that these features would have been inherent in the combined disclosures of the prior art and that a person skilled in the art would understand the features to be inherent. *Id.* The Court of Appeals for the Federal Circuit reversed the Examiner's conclusion of obviousness, stating that, as a matter of law, "a retrospective view of inherency is not a substitute for some teaching or suggestion supporting an obviousness rejection." *Id.* The Court held that obviousness cannot be shown based on what is not known in the prior art at the time an invention is made, even if the inherency of a certain feature is later established. *Id.*; see also MPEP § 2141.02.V.

Here, the distinctive aluminum-rich oxide scale comprising aluminum, chromium, and iron, and having a particular hematite structure, as recited in claims 1 and 10, was not known in the prior art at the time the methods recited in claims 1 and 10 were made. Therefore, an obviousness rejection cannot be supported by the prior art, even if the distinctive aluminum-rich oxide scale would be inherent. Furthermore, Ishibashi teaches a chemically and structurally different oxide. As such, the Examiner has not established a *prima facie* case of obviousness. *In re Rijckaert*, 9 F.3d 1531; MPEP § 2141.02.V.

The law governing obviousness under 35 U.S.C. § 103(a) requires that allegedly inherent features be taught or suggested in the prior art in order to

support a case of *prima facie* obviousness. This well-settled principle of law is supported by a number of cases. See, e.g., *In re Spormann*, 363 F.2d 444, 448 (CCPA 1966) ("...the inherency of an advantage and its obviousness are entirely different questions. That which may be inherent is not necessarily known. Obviousness cannot be predicated on what is unknown."); *W.L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 1555 (Fed. Cir. 1983) ("Inherency and obviousness are distinct concepts."); *Kloster Speedsteel AB v. Crucible Inc.*, 793 F.2d 1565, 1576 (Fed. Cir. 1986) (an inherent feature may be relied upon to establish obviousness only if the inherency itself would have been obvious to a person skilled in the art); *Cohesive Technologies Inc. v. Waters Corp.*, 543 F.3d 1351 (Fed. Cir. 2008) ("...although anticipation can be proven inherently, proof of inherent anticipation is not the same as proof of obviousness.").

Indeed, this principle of law is so well-settled that it is stated in a preeminent treatise on United States patent law. See 2 Donald S. Chisum, *Chisum on Patents* § 5.03[3][a][i][A] (Matthew Bender) (a single prior art reference may anticipate because of the inherent disclosure of the reference, but inherent disclosure may only be used to support obviousness if the inherent subject matter itself would have been obvious, i.e., taught or suggested in the prior art).

In addition, in the case of *In re Newel*, 891 F.2d 899 (Fed. Cir. 1989), the examiner also based an obviousness rejection on a combination of prior art references that failed to teach or suggest certain features recited in the rejected claims, arguing that the missing subject matter would have been inherent in the prior art. Again, the Court of Appeals for the Federal Circuit reversed the examiner's conclusion of obviousness, holding that, as a matter of law, the examiner cannot use an unsupported inherency argument as an end-run around the requirement for a teaching or suggestion of the asserted inherent feature in the prior art. *Id.* The Court held that extrinsic prior art evidence is

required to support an asserted inherency argument in an obviousness rejection.  
*Id.*

Thus, the case law makes it abundantly clear that obviousness rejections based on asserted "inherent" properties in the art cannot be sustained when there is no teaching or suggestion in the prior art to support the assertedly inherent subject matter. *In re Spormann, supra; In re Rijckaert, supra.* When the Examiner asserts that there is an inherent feature in the prior art, the Examiner must produce supporting references that teach or suggest the allegedly inherent subject matter. *In re Newell, supra.*

In the present case, the Examiner has failed to cite to any prior art or other evidence whatsoever that teaches or suggests the formation of an aluminum-rich, oxidation resistant oxide scale comprising aluminum, chromium, and iron, and having a particular hematite structure, as recited in claims 1 and 10. In fact, Ishibashi teaches a different oxide altogether. Therefore, Ishibashi cannot serve as the basis for a *prima facie* case under 35 U.S.C. § 103(a).

Moreover, to establish inherency, the extrinsic evidence (*i.e.*, the cited reference) must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by a person skilled in the art. *In re Robertson*, 169 F.3d 743, 745 (Fed. Cir. 1999); MPEP § 2112.IV. Inherency may not be established by probabilities or possibilities; inherency requires factual evidence of an alleged inherent feature. *Id.* In this regard, MPEP § 2112.IV provides that:

'In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art.' *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990) (emphasis in original).

Accordingly, in order for the aluminum-rich oxide scale recited in the claims of the Subject Application to have been inherent, as asserted by the Examiner,

the particular chemistry, crystal structure, and properties of the scale must necessarily exist in the disclosure of Ishibashi, and have been identifiable by a person skilled in the art. In the present case, however, the distinctive aluminum-rich oxide scale recited in claims 1 and 10 of the Subject Application is not taught or suggested in Ishibashi. Further, the aluminum-rich oxide scale recited in claims 1 and 10 would not have been expected as an inherent property by a person skilled in the art. See the Declaration of Michael P. Brady, Ph.D., submitted in the Subject Application on August 23, 2007, which provides independent expert testimony that the features recited in the present claims would have been unexpected before the Subject Application.<sup>2</sup>

Therefore, the Examiner's unsupported assertion that the recited oxide scale would have been inherent is a conclusory statement that cannot form the basis of a *prima facie* case under 35 U.S.C. § 103(a).

iv. **Ishibashi does not teach or suggest the critical levels of aluminum and rare earth metals recited in claims 1, 10, and 11.**

As described in the Specification, 0.2 to 1.0 weight percent aluminum, and from 0.02 to 1.0 weight percent of at least one rare earth metal, is critical for the development of the distinctive aluminum-rich oxide scale on the electropolished surfaces of ferritic stainless steels and the resulting high temperature oxidation resistance properties. See *Specification*, Example 4, ¶¶ [0069]-[0073]. Ishibashi does not teach or suggest providing a ferritic stainless steel comprising these critical levels of aluminum and rare earth metals, as recited in claims 1, 10, and 11.

In contrast, Ishibashi discloses steel compositions that may include 0.001 to 5.00 weight percent aluminum and 0.001 to 5.00 weight percent yttrium. *Ishibashi*, abstract. Thus, the chemistry of the stainless steel compositions disclosed in Ishibashi is extremely broad. Indeed, Ishibashi expressly acknowledges that the disclosed

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<sup>2</sup> The Declaration of Michael P. Brady, Ph.D., submitted August 23, 2007, is included in the *Evidence Appendix, infra*, and discussed in greater detail in *Section C.5, infra*.

stainless steels may be either ferritic or austenitic. *Ishibashi*, c.3, II.50-54. The alloy chemistry recited in the claims of the Subject Application is significantly narrower as compared to the broad and unspecific chemistry disclosed in *Ishibashi*. Furthermore, there is no disclosure in *Ishibashi* that would lead a person skilled in the art to experiment, optimize, or otherwise determine the critical ranges for aluminum and rare earth elements, as recited in claims 1, 10, and 11.

Nevertheless, the Examiner asserts that it would have been obvious to select the claimed narrow ranges of aluminum and rare earth elements from the broad ranges of aluminum and yttrium disclosed in *Ishibashi* because *Ishibashi* "discloses the same utility throughout the disclosed ranges." *Office Action* issued November 23, 2009, p.4. Appellant respectfully disagrees because *Ishibashi* does not disclose any utility for aluminum and yttrium, let alone the same utility as described in the Specification.

In a section having the sub-heading "Metal Composition", *Ishibashi* describes the chemical composition of the metal alloys that may be used to produce the solar collector disclosed in the document. See *Ishibashi*, c.3, I.27-c.4, I.21. Aluminum and the rare earth metal yttrium are described in *Ishibashi* in two instances, c.3, II.61-62 and c.4, II.15-16, reproduced below (emphases added).

Another one of the metal compositions used in the 55 present invention is the stainless steel having low carbon content compounding other metal to improve the anticorrosion, the formability and the weldability, for example, 0.001 - 0.15 wt % of C, 0.005 - 3.00 wt % of Si, 0.005 - 10.00 wt % of Mn, 11.00 - 30.00 wt % of Cr 60 and 0.001 - 5.00 wt % of at least one of element(s) selected from the group of N, Cu, Al, V, Y, Ti, Nb, Ta, U, Th, W, Zr and Hf, optionally, 0.75 - 5.00 wt % of Mo and the balance being of Fe, Me/C + N ratio being more than 5.0, while said ratio being more than 8.0 in 65 the stainless steel comprising Nb, Ta, or Ti as the additional element.

Further another one of the metal compositions used in the present invention is the stainless steel having low carbon content compounding other metal to improve the anticorrosion, the formability and the weldability, for example 0.001 – 0.15 wt % of C, 0.005 – 3.00 wt % of Si, 0.005 – 10.00 wt % of Mn, 0.005 – 22.00 wt % of Ni, 11.00 – 30.00 wt % of Cr and 0.001 – 5.00 wt % of at least one of element(s) selected from the group of N, Cu, Al, V, Y, Ti, Nb, Ta, U, Th, W, Zr and Hf, optionally, 0.75–5.00 wt % of Mo and the balance being of Fe, Me/C + N ratio being more than 5.0, while said ratio being more than 8.0 in the stainless steel comprising Nb, Ta, or Ti as the additional element.

Thus, Ishibashi discloses aluminum and yttrium among an unspecific and undifferentiated list of thirteen alloying elements that may be present in stainless steels in concentrations ranging from 0.001 to 5.00 weight percent. Ishibashi provides absolutely no teachings related to the utility of any of these elements, let alone aluminum and yttrium specifically. Therefore, the Examiner's assertion that Ishibashi "discloses the same utility throughout the disclosed ranges" is incorrect. Ishibashi does not describe any utility for aluminum and yttrium, whatsoever, let alone that certain narrow concentrations of these elements are necessary for the development of certain oxide scales on electropolished surfaces exposed to high temperature oxidizing atmospheres.

The Specification shows that 0.2 to 1.0 weight percent aluminum, and 0.02 to 1.0 weight percent of at least one rare earth metal, is critical for the formation of the distinctive aluminum-rich oxide scale on the electropolished surfaces of ferritic stainless steels and the significant improvement in high temperature oxidation resistance. See *Specification*, ¶ [0071] (describing aluminum), and ¶ [0072] (describing rare earth metals). These narrower concentrations correlate with unexpected results, i.e., the distinctive aluminum-rich oxide scale that develops on the electropolished surfaces of ferritic stainless steels and the significant improvement in high temperature

oxidation resistance properties, which are not taught or suggested in the cited prior art. A person skilled in the art would not have found it obvious to select these critical narrow ranges from the broad 0.001 to 5.00 weight percent described in Ishibashi for alloying elements that do not have any disclosed utility whatsoever. Indeed, a person skilled in the art would have had no basis in technological fact to identify and select the narrow ranges from the broader ranges given that the prior art does not identify any utility for aluminum and rare earth metals, let alone the distinctive oxide scale and the significant improvement in the high temperature oxidation resistance, recited in claims 1, 10, and 11.

The Examiner apparently asserts that a *prima facie* case of obviousness is established, relying on MPEP § 2144.05(I) and the cases cited therein as a legal basis for the § 103(a) rejections. Appellant respectfully disagrees.

First, Appellant notes that the MPEP does not have the force and effect of law regarding patentability; the MPEP merely provides a useful collection of the controlling legal authority, *i.e.*, the case law governing patentability. See *Molins PLC v. Textron, Inc.*, 48 F.3d 1172, 1180 n.10 (Fed. Cir. 1995) (*citing Litton Sys., Inc. v. Whirlpool Corp.*, 728 F.2d 1423, 1439 (Fed. Cir. 1984); *McKesson Information Solutions, Inc. v. Bridge Medical, Inc.*, 487 F.3d 897, 923 n.2 (Fed. Cir. 2007) (*citing Refac Int'l Ltd. v. Lotus Development Corp.*, 81 F.3d 1576, 1584 n.2 (Fed. Cir. 1996))). Thus, the MPEP is only determinative to the extent that it is consistent with the holdings and precedents of the cited case law.

Section 2144.05(I) of the MPEP provides that in a case where the claimed ranges overlap or lie inside ranges disclosed by the prior art a *prima facie* case of obviousness exists. While these MPEP passages, considered in isolation, arguably support the Examiner's rejections, a review of the underlying cases reveals that the present case involving the Subject Application is readily distinguishable.

In the cases cited in MPEP § 2144.05(I) in which a *prima facie* case of obviousness was found based on overlapping ranges, the overlap was substantial

and/or the prior art range was relatively narrow. See, e.g., *In re Wertheim*, 541 F.2d 257 (CCPA 1976) (claimed ranges of 0.4-0.8 gm/cc and 28-60% solids content held obvious in view of prior art 0.1-0.5 gm/cc and 30% solids); *In re Woodruff*, 919 F.2d 1575 (Fed. Cir. 1990) (claimed range of 5-25% carbon monoxide held obvious in view of prior art 1-5% carbon monoxide); *Titanium Metals Corp. of America v. Banner*, 778 F.2d 775 (Fed. Cir. 1985) (claimed titanium alloy having 0.8% Ni and 0.3% Mo held obvious in view of two (2) prior art titanium alloys, one having 0.75% Ni and 0.25% Mo, and the other having 0.94% Ni and 0.31% Mo). In each of these cases, the claimed ranges or the specific compositions very closely approximated those disclosed in the prior art. Indeed, in most of the cases the claimed ranges were substantially broader than the ranges disclosed in the prior art.

In the present case, however, the concentrations recited in the claims of the Subject Application are substantially narrower as compared to what is disclosed in Ishibashi. Indeed, Ishibashi describes ranges that are extremely broad and encompass a vast number of different stainless steels – both austenitic and ferritic. In order to arrive at the methods recited in the claims of the Subject Application, it would have required extensive research and experimentation over all of the numerous broad ranges disclosed in Ishibashi. Moreover, it would also have required an identification of the distinctive scale and oxidation resistance parameters (and their correlation to electrochemical modification) used to develop the method recited in the present claims, which are not taught or suggested in Ishibashi. Consequently, starting with Ishibashi, a person skilled in the art would not have been able to achieve the methods recited in the present claims by the mere application of ordinary skill. Rather, it would have required achieving an inventive step over and above the disclosure in Ishibashi. For that reason, among others, the Examiner cannot rely on the mere presence of overlap alone as the basis for an obviousness rejection.

Moreover, MPEP § 2144.05.I states that if a cited reference's disclosed range is so broad as to encompass a very large number of possible distinct compositions, "this might present a situation analogous to the obviousness of a species



when the prior art broadly discloses a genus." *In re Peterson*, 315 F.3d 1325, 1330 (Fed. Cir. 2003); *In re Baird*, 16 F.3d 380 (Fed. Cir. 1994); *In re Jones*, 958 F.2d 347 (Fed. Cir. 1992); MPEP § 2144.08. Such a situation exists here because Ishibashi very broadly and unspecifically discloses aluminum and yttrium concentrations, but does not suggest that specific aluminum and rare earth metal concentrations are productive of unexpected results as achieved by the present claimed invention (*i.e.*, a distinctive oxide scale and significant improvement in high temperature oxidation resistance, as recited in claims 1, 10, and 11).

Although ranges in the prior art that are not especially broad may invite routine experimentation to discover optimum values where appropriate result effective variables are identified in the prior art (*see* MPEP § 2144.05.II), here Appellant submits that:

- the ranges disclosed in Ishibashi are so broad and unspecific that it would require non-obvious invention to arrive at the ranges recited in the claims of the Subject Application (*In re Peterson*, 315 F.3d 1325, n.1); and
- Ishibashi fails to identify any result effective variable that could be optimized to arrive at the ranges recited in the claims of the Subject Application (MPEP § 2144.05.II).

The Examiner also argues that the normal desire of scientists or artisans to improve upon what is already known provides the motivation to determine where in a disclosed set of percentage ranges is the optimum combination of percentages, citing to MPEP § 2144.05.II). In this regard, the Examiner asserts that it would have been obvious to optimize the 0.001 to 5.0 weight percent aluminum and yttrium ranges disclosed in Ishibashi in order to determine the 0.2 to 1.0 weight percent aluminum range and the 0.02 to 1.0 weight percent rare earth metal range, as recited in claims 1, 10, and 11.

However, there is no suggestion in Ishibashi that aluminum and yttrium concentration correlate to any recognized result that may be optimized, let alone correlating aluminum and yttrium concentration to oxidation resistance and the development of a distinctive oxide scale on electropolished surfaces under oxidizing

conditions. As stated in MPEP § 2144.05(II)(B), "[a] particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation." Therefore, the Examiner's optimization argument is improper because Ishibashi does not recognize aluminum and yttrium concentrations as achieving any recognized result. Thus, a person skilled in the art would not have any technological basis to perform the optimization asserted by the Examiner to arrive at the methods recited in the present claims.

As stated in MPEP § 2144.08, the patentability of a claim to a specific compound or subgenus of compounds embraced by a prior art genus should be analyzed no differently than any other claim for purposes of § 103(a). MPEP § 2144.08 further states the following, with citation to controlling case law on the issue:

The fact that a claimed species or subgenus is encompassed by a prior art genus is not sufficient by itself to establish a *prima facie* case of obviousness. *In re Baird*, 16 F.3d 380, 382 ... (Fed. Cir. 1994) ('The fact that a claimed compound may be encompassed by a disclosed generic formula does not by itself render that compound obvious.');

*In re Jones*, 958 F.2d 347, 350 ... (Fed. Cir. 1992) (Federal Circuit has 'decline[d] to extract from *Merck & Co. v. Biocraft Laboratories Inc.*, 874 F.2d 804 ... (Fed. Cir. 1989)] the rule that ... regardless of how broad, a disclosure of a chemical genus renders obvious any species that happens to fall within it.'). See also *In re Deuel*, 51 F.3d 1552, 1559 ... (Fed. Cir. 1995).

Here, given that Ishibashi broadly discloses aluminum and yttrium among an undifferentiated list of thirteen elements, with no specific utility for any of the elements, there is no rational basis upon which a person skilled in the art would have found it obvious to electropolish a particular ferritic stainless steel having aluminum and rare earth metal in the narrowly recited concentration ranges in order to electrochemically modify the surface of the steel so that it develops a distinctive aluminum-rich oxide scale providing a significant improvement in high temperature oxidation resistance, as recited in claims 1, 10, and 11.

Therefore, the disclosure presented in Ishibashi cannot form the basis of a *prima facie* case under 35 U.S.C. § 103(a).

**v. Ishibashi does not teach or suggest an  
uncoated electropolished oxidation resistant  
surface as recited in claim 11.**

As noted above, claims 1 and 10 each include the feature wherein, under certain conditions, an exposed electropolished surface of a ferritic stainless steel develops a distinctive aluminum-rich oxide scale comprising chromium and iron and having a hematite structure. In order for an electropolished surface of a ferritic stainless steel to develop an oxide scale, the chemical elements that constitute the electropolished surface of the alloy must react with oxygen in an oxidizing atmosphere. For this to occur, the electropolished surface must remain exposed to the surrounding oxidizing atmosphere – otherwise the oxygen would be physically and chemically blocked from reacting with the constituent chemical elements of the electropolished surface and an oxide scale could not develop. In order to remain exposed to the surrounding atmosphere, an electropolished surface of a ferritic stainless steel article cannot be coated. In this regard, claim 11 explicitly provides that the electropolished surface is uncoated.

Nevertheless, the Examiner maintains that claims 1, 10, and 11 would have been obvious in view of Ishibashi, which teaches mechanically polishing, chemically abrading, and electropolishing to flatten the surface of a stainless steel substrate (c.7, ll. 34-42), and then adhering an oxide coating layer to the flattened, mirror-like surface of the substrate (abstract). The oxide coating layer is adhered to the substrate using one of four techniques described in Ishibashi at column 4, lines 26-45 and column 8, lines 10-25. Thus, the mechanically polished, chemically abraded, and electropolished surface of the substrate in Ishibashi is not left exposed to develop an oxide scale, but instead is actively coated with a layer of a metal oxide material.

The Examiner argues that the present claims recite the transitional phrase "comprising" and, therefore, are allegedly open to a coating step. However, as discussed above, a coating step would block the electropolished surface from reacting with oxygen to develop the recited oxide scale, which would eliminate this feature from

the claims. The Examiner must consider all of the words and features recited in a claim in judging the patentability of the claim against the prior art. See MPEP § 2143.03. The Examiner cannot interpret a claim so that a recited feature is eliminated. The present claims include the following features:

- an exposed electropolished surface of a ferritic stainless steel that, under certain conditions, develops an aluminum-rich oxide scale comprising chromium and iron and having a hematite structure; and/or
- an uncoated electropolished surface.

These features are not technologically possible with a coated surface as described in Ishibashi. Accordingly, the methods recited in the present claims would not have been obvious in view of Ishibashi.

The Examiner further argues that an intermediate product of Ishibashi would be an electropolished and uncoated ferritic stainless steel, which allegedly meets the present claims. However, this argument is inconsistent with the requirement that prior art references must be considered in their entirety, *i.e.*, as a whole, including portions that would lead away from the claimed invention. See MPEP § 2141.02.VI.

Ishibashi emphasizes the importance of the coating layer adhered to the underlying steel substrate, which provides superior spectroscopic characteristics and absorption properties as a solar collector material. *Ishibashi*, c.13, ll.44-63. In this regard, the object and purpose of the invention disclosed in Ishibashi is to provide a selective absorption surface for a solar collector using a metal oxide coating. *Id.* at c.2, ll.39-44. Accordingly, the electropolished intermediate product of Ishibashi, *i.e.*, lacking the applied coating, is unsatisfactory for its intended purposes and changes the principle of operation of the invention disclosed in Ishibashi. Therefore, the teachings of Ishibashi are not sufficient to render claim 11 *prima facie* obvious. See *In re Gordon*, 733 F.2d 900 (Fed. Cir. 1984); *In re Ratti*, 270 F.2d 810 (CCPA 1959); MPEP § 2143.01.V-VI.

The Examiner's argument regarding the intermediate product of Ishibashi proposes a modification to eliminate the coating layer because otherwise the disclosed mirror-like surface of the substrate would be coated as described in Ishibashi. In other words, if the substrate is coated as described in Ishibashi, then it cannot form an oxide scale, and if the substrate is uncoated, then the invention described in Ishibashi is rendered inoperable for its intended purpose. Ishibashi does not teach or suggest electropolishing an exposed or uncoated surface, let alone electropolishing to chemically modify an exposed or uncoated surface so that the surface will develop an oxidation resistant scale as recited in the claims of the Subject Application.

In Ishibashi, the substrate surface is purposefully coated with a relatively thick coating of a predetermined material. Given that fact, Appellant submits that the underlying electropolished substrate surface could not possibly develop an oxide scale having the features recited in claims 1, 10, and 13, for example. As a result, Ishibashi cannot teach or suggest – inherently or otherwise – the scale having the structure recited in the claims of the Subject Application because the exposed surfaces of the Ishibashi solar reflector are coated with a predetermined material. This would prevent the formation of a scale having the features recited in the claims of the Subject Application.

For at least the foregoing reasons, the methods recited in claims 1-5, 9-11, 13, 16, 18, 20-22, and 26 would not have been obvious in view of Ishibashi. Therefore, Appellant respectfully requests reversal of the rejections under § 103(a) based on Ishibashi.

**3. Independent claims 1, 10, 11, and 99 would not have been obvious over Szummer in view of Ono, Linden, Uematsu, or Matsui.**

The Examiner asserts that claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 would have been obvious over Szummer in view of Ono, Linden, Uematsu, or

Matsui (the "secondary references"), in the alternative. Appellant respectfully disagrees for at least the following reasons.

i. **The scope and content of the prior art – the teachings of Szummer and the secondary references.**

Szummer describes using electropolishing to prepare ferritic stainless steel specimens for studying the "surface microstructure of ferritic chromium stainless steels subjected to hydrogen charging". *Szummer*, abstract. In this regard, Szummer states that (*id.* at p.356, c.2):

After cutting, the specimens were first mechanically polished and then electropolished .... TEM specimens were prepared by preliminary electrolytic thinning without perforation, then cathodically charged and thinned from one side by electrochemical polishing until perforation. The H-charged surface was left unaffected by the preparation procedure so that the H-induced microstructural changes in the sample could be examined ... using optical, scanning and transmission electron microscopes ....

Szummer does not teach any aluminum or rare earth metal content, and the Examiner cites the secondary references, in the alternative, for the disclosure of a ferritic stainless steel including aluminum and rare earth metals. The Examiner asserts that it would have been obvious to add the aluminum and rare earth metals, as disclosed in the secondary references, to the ferritic stainless steel disclosed in Szummer, in order to:

- ...improve oxidation (corrosion) resistance, as disclosed by Ono...;
- ...form a protective oxide layer and improve adhesion of the oxide layer, as disclosed by Linden...;
- ...maintain high temperature oxidation resistance and improve adhesion of the oxide film, as disclosed by Uematsu...; and
- ...maintain high temperature oxidation resistance and improve adhesion of the oxide film, as disclosed by Matsui....

Office Action issued November 23, 2009, pp. 8, 14, 19, and 24, respectively. However, there is no disclosure in Szummer or the secondary references related to electrochemical modification of ferritic stainless steels.

ii. **Szummer in view of Linden and Uematsu.**

Linden and Uematsu teach 3-20 weight percent aluminum and 1-4.5 weight percent aluminum, respectively. In contrast, claims 1, 10, and 11 recite 0.2 to 1.0 weight percent aluminum, and claim 99 recites 0.4 to 0.8 weight percent aluminum. Thus, the aluminum concentrations disclosed in Linden do not overlap with any of the aluminum concentration ranges recited in the claims of the Subject Application. Likewise, the aluminum concentrations disclosed in Uematsu do not overlap with the aluminum concentration range recited in claim 99. Accordingly, the Examiner cannot rely on MPEP § 2144.05 to establish a *prima facie* case of obviousness. Therefore, Appellant respectfully submits that the rejections under § 103(a) based on Szummer in view of Linden, and Szummer in view of Uematsu, are improper and must be reversed.

iii. **The Examiner's asserted reasons for combining Szummer with the secondary references are improper.**

Appellant respectfully submits that the asserted reasons for combining Szummer with the secondary references are merely conclusory statements and do not possess a rational underpinning to support a legal conclusion of obviousness. *See Ex Parte Linzer*, Appeal 2009-001858, \*6 (BPAI May 28, 2010) (citing *In re Kahn*, 441 F.3d 977, 998 (Fed. Cir. 2006), quoted in *KSR Int'l Co. v. Teleflex Inc.*, 550 U.S. 398, 418 (2007)).

Szummer generally describes a metallographic study of the surface microstructure of ferritic stainless steels after hydrogen charging. *Szummer*, abstract. To perform the study, ferritic stainless steel specimens were first mechanically polished, then electropolished, then hydrogen was introduced into the surface of the polished

samples by cathodic charging, and then the hydrogen-charged surfaces were examined using various forms of microscopy. *Id.* at p.356, c.2. It is well known in the art of metallographic examination that electropolishing is used to prepare metallic samples for microscopic examination. In the ASM Materials Engineering Dictionary, electropolishing is defined as:<sup>3</sup>

A technique commonly used to prepare metallographic specimens, in which a high polish is produced making the specimen the *anode* in an *electrolytic cell*, where preferential dissolution at high points smooths [*sic*] the surface. Also referred to as *electrolytic polishing*. (Emphases in original.)

Electrolytic polishing, in turn, is defined as:<sup>4</sup>

An electrochemical polishing process in which the metal to be polished is made the *anode* in a electrolytic cell where preferential dissolution at high points in the surface topography produces a specularly reflective surface ... Also referred to as *electropolishing*. (Emphases in original.)

There are various reasons that electropolishing is used in metallography (*i.e.*, as it is used in Szummer) to prepare specimens of metallic samples for optical and electron microscopic surface analyses. Firstly, the electropolished surface is highly smooth and reflective. This facilitates detection of second phases in the microstructure of the metal or metal alloy. Secondly, for examination at higher magnifications, such as when using transmission electron microscopy (TEM), electropolishing is used to thin metal specimens to a thickness where the electrons from the TEM can penetrate the thinned metal specimens to image (and chemically analyze) the thin specimens. Thirdly, electropolishing removes surface oxides from the specimen, thereby revealing the underlying metal alloy.<sup>5</sup>

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<sup>3</sup> ASM Materials Engineering Dictionary, Fifth Printing, J. R. Davis ed., ASM International (2006), p. 141, emphases in original (copies of the relevant pages are included in the *Evidence Appendix, infra*).

<sup>4</sup> *Id.* at 139, emphases in original.

<sup>5</sup> See Metallographic Practices for Wrought Stainless Steels in ASM Specialty Handbook® of Stainless Steels, J. R. Davis ed., ASM International (1994), p. 440-444 (copies of the relevant pages are included in the *Evidence Appendix, infra*).



As described in Szummer, electropolishing is used to provide a smooth, reflective, and oxide-free alloy surface that is hydrogen-charged to study the effects of the hydrogen charging on the microstructure of the alloy material, not on oxide structure. Indeed, Szummer expressly states that the hydrogen-charged surfaces of the specimens were "left unaffected by the preparation procedure so that the H-induced microstructural changes in the sample surface zones could be examined." *Szummer*, p.356, c.2. Thus, the purpose of the study described in Szummer was to investigate the microstructure of hydrogen-charged metallic alloy. The Examiner's asserted reasons for combining Szummer with the secondary references and modifying the chemical composition of the alloy described in Szummer are inconsistent with this study.

For example, the Examiner asserts that the combination of Szummer and Ono would have been obvious in order to improve oxidation (corrosion) resistance. However, there is no advantage to improving the oxidation resistance of the specimens studied in Szummer because the purpose of the study is to investigate the effects of hydrogen. Indeed, Appellant submits that modifying Szummer as asserted by the Examiner would introduce additional variables into the disclosed study, which could confound the variables investigated in the study. A person skilled in the art would not add additional, unnecessary variability into a controlled study, as asserted by the Examiner.

Likewise, the Examiner asserts that the combination of Szummer and Linden, Uematsu, or Matsui would have been obvious in order to form a protective oxide layer, improve adhesion of the oxide layer, and maintain high temperature oxidation resistance. However, as noted above, the investigators performing the study described in Szummer used polishing and electropolishing to remove surface oxides in order to charge the alloy surface with hydrogen and perform microscopic analysis of the hydrogen-charged surfaces. Modifying the study described in Szummer in order to increase the formation and adhesion of an oxide layer would be counterproductive to the performance of the disclosed study because it would be more difficult to produce smooth, reflective, and oxide-free alloy surfaces for hydrogen-charging and microscopy.

Further, modifying Szummer to promote oxide formation would also introduce additional variables into the disclosed study, which could confound the variables investigated in the study. Again, a person skilled in the art would not add additional, unnecessary variability into a controlled study, as asserted by the Examiner.

Therefore, the Examiner's reasons for combining Szummer with the secondary references are mere conclusory statements that are technologically inconsistent with the teachings of Szummer and, therefore, cannot establish *prima facie* cases of obviousness. See *Ex Parte Linzer*, Appeal 2009-001858, \*6.

iv. **The cited references do not teach or suggest electropolishing to make a ferritic stainless steel article having an oxidation resistant surface.**

Szummer in view of the secondary references does not teach or suggest electropolishing as a step in a "method for making a ferritic stainless steel article having an oxidation resistant surface", as recited in claims 1, 10, 11, and 99. In fact, Szummer in view of the secondary references lacks any teaching, suggestion, or motivation whatsoever to use electropolishing on a ferritic stainless steel alloy comprising controlled levels of 0.2 to 1.0 weight percent aluminum and 0.02 to 1.0 weight percent total rare earth metal, in order to produce an oxidation resistant surface as recited in claims 1, 10, 11, and 99.

As noted above, the metallographic art of electropolishing stainless steels for microscopic examination is a conventional sample preparation technique. Szummer merely discloses the use of electropolishing in this manner, and there is absolutely no reason why a person skilled in the art would look to Szummer to develop a "method for making a ferritic stainless steel article having an oxidation resistant surface". Szummer merely mentions electropolishing ferritic stainless steels for metallographic analysis; there is no teaching or suggestion that electropolishing would be an effective means to prepare an oxidation resistant surface on ferritic stainless steel, let alone teaching or suggesting a particular oxide crystal structure. Likewise, the secondary references do

not teach or suggest the critical aluminum and rare earth metal contents recited in claims 1, 10, 11, and 99.

As part of the determination of the scope and content of the prior art, prior art references must be considered in their entirety. MPEP § 2141.02(VI) (case law citations omitted). Assuming, for sake of argument only, that a person skilled in the art was considering Szummer and any one of the secondary references, that person, at most, may recognize a method for studying the surface microstructure of the ferritic stainless steel disclosed in the secondary reference after being subjected to hydrogen charging. However, given the lack of any disclosure in the cited references relating to electrochemical modification resulting in distinctive oxide scale formation under high temperature oxidizing conditions, the person skilled in the art would not recognize as obvious "a method for making a ferritic stainless steel article having an oxidation resistant surface" and including specific elemental concentrations, as recited in claims 1, 10, 11, and 99.

As a result, Szummer and the secondary references cannot establish a *prima facie* case of obviousness under 35 U.S.C. § 103(a).

- v. **The aluminum-rich oxide scale recited in independent claims 1, 10, and 99 would not have been inherently expected from the disclosure presented in Szummer and the secondary references.**

The Examiner acknowledges that metallographic sample preparation for studying hydrogen charging effects would be the result of Szummer modified in view of the secondary references. *Office Action* issued November 23, 2009, p.34. Nevertheless, the Examiner maintains that a person skilled in the art would expect that the electropolished steel of Szummer in view of the secondary references would have the same features as recited in the present claims because, allegedly, the same process is conducted on substantially the same composition. But, the Examiner does not explain why or how a person skilled in the art would expect this considering that

Szummer does not recognize any effect of electropolishing on high temperature oxidation resistance, let alone resulting in a chemical modification that results in the development of a distinct aluminum-rich oxide scale.

Here, the Examiner is again apparently arguing that the high temperature oxidation resistance feature and the aluminum-rich oxide scale feature recited in the present claims would be inherent in Szummer in view of the secondary references, regardless of whether the cited references recognize these features. However, as set forth in MPEP § 2141.02(V), "obviousness cannot be predicated on what is not known at the time an invention is made, even if the inherency of a certain feature is later established." Rather, in order to rely on some allegedly inherent feature of the prior art when establishing a *prima facie* case of obviousness, the allegedly inherent feature must have been taught or suggested in the prior art at the time that the claimed invention was made. *In re Rijckaert*, 9 F.2d 1531.

As discussed in detail in *Section C.2.ii, supra*, the controlling case law makes it abundantly clear that obviousness rejections based on asserted "inherent" properties in the art cannot be sustained when there is no teaching or suggestion in the prior art to support the assertedly inherent subject matter. *In re Spormann, supra; In re Rijckaert, supra*. When the Examiner asserts that there is an inherent feature in the prior art, the Examiner must produce supporting references that teach or suggest the allegedly inherent subject matter. *In re Newell, supra*.

In the present case, the Examiner has failed to cite to any prior art or other evidence whatsoever that teaches or suggests the formation of an aluminum-rich oxide scale comprising aluminum, chromium, and iron, and having a particular hematite structure, as recited in claims 1, 10, and 99. In fact, Szummer teaches removing oxides and charging steel surfaces with hydrogen. The secondary references do not remedy this deficiency. Further, the distinctive aluminum-rich oxide scale recited in independent claims 1, 10, and 99 would not have been expected as an inherent property by a person skilled in the art. See the Declaration of Michael P. Brady, Ph.D., submitted August 23,

2007, which provides independent expert testimony that the features recited in the present claims would have been unexpected before the Subject Application.<sup>6</sup>

Therefore, a *prima facie* case of obviousness has not been established. MPEP § 2141.02(V). A method for studying the surface microstructure of ferritic stainless steels after hydrogen charging (as taught by Szummer, alone or in view of the secondary references) would not render obvious a method for making a ferritic stainless steel article having an oxidation resistant surface that develops a distinctive aluminum-rich oxide scale under high temperature oxidation conditions (as recited in the present claims), "even if the inherency of a certain feature is later established." MPEP § 2141.02(V). The Examiner provides no evidence that the composition and hematite structure of the recited oxide scale, let alone the particular lattice parameters, were known or recognizable when the claimed invention was made. The Examiner admits that these features are not taught or suggested in the cited references. Therefore, the obviousness rejections based on inherency are improper.

Therefore, the Examiner's unsupported assertion that the recited oxide scale would have been inherent is a conclusory statement that cannot form the basis of a *prima facie* case under 35 U.S.C. § 103(a).

#### **4. Unexpected results.**

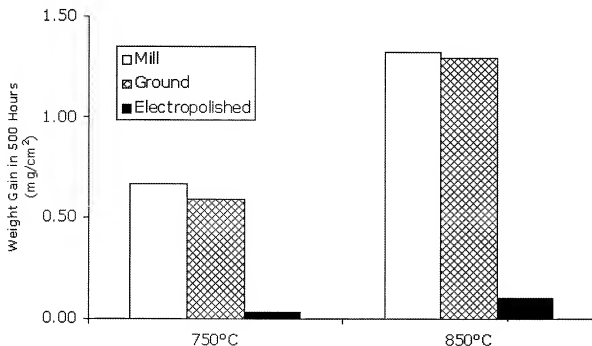
As discussed above, the Examiner has not established a *prima facie* case that the subject matter recited in any of independent claims 1, 10, 11, and 99 would have been obvious. In addition, Appellant respectfully submits that the data provided in the Specification provides sufficient evidence of unexpected results given the total lack of teachings in the cited art regarding: (1) an electrochemical modification effect due to electropolishing ferritic stainless steels; (2) the development of a distinctive aluminum-

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<sup>6</sup> The Declaration of Michael P. Brady, Ph.D., submitted August 23, 2007, is included in the *Evidence Appendix, infra*, and discussed in greater detail in *Section C.5, infra*.

rich oxide scale; and (3) a significant improvement in high temperature oxidation resistance.

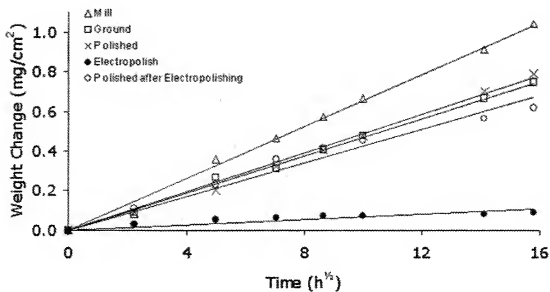
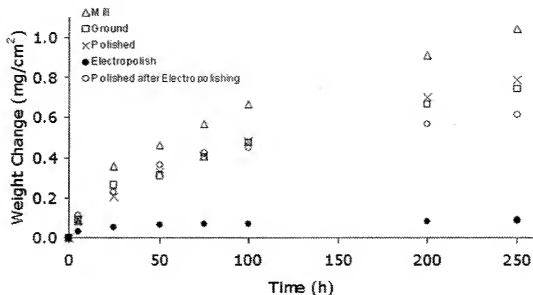
Example 1 in the Specification (¶¶ [0052]-[0058]) shows that the rate of high temperature oxidation of electropolished samples of a ferritic stainless steel having a composition that falls within the recited compositional ranges was several orders of magnitude lower than that of otherwise identical non-electropolished samples. This significant reduction was unexpected and surprising because there is no disclosure in the prior art that teaches or suggests such an improvement in high temperature oxidation resistance due to electropolishing. Figure 5 of the Subject Application, reproduced below, shows that the electropolished samples oxidized at a substantially lower rate than the non-electropolished samples.



This data is confirmed by the parabolic rate constants ( $k_p$ ) for the oxidations, which indicate that the rate of oxidation of the electropolished samples was several orders of magnitude lower than that of the mechanically finished mill and ground

(but otherwise identical) samples with a corresponding reduction in final specific weight change due to oxidation of about an order of magnitude. See *Specification*, ¶ [0056]. Further, the non-electropolished mill and ground samples formed a charcoal-grey colored oxide scale characteristic of standard chromium-rich oxides generally observed for stainless steels, whereas the electropolished (but otherwise identical) samples formed a transparent golden colored oxide through which the original metal surface was visible. *Id.* at [0055]. This golden colored oxide is the distinctive aluminum-rich oxide scale comprising chromium and iron and having a hematite structure, as recited in the claims of the Subject Application. *Id.* at [0058]. Moreover, this unexpected, significant, and distinctive aluminum-rich oxide scale, and the unexpected and significant improvement in high temperature oxidation resistance, were confirmed by a second set of independent oxidation tests. *Id.* at ¶ [0057]; Figure 4.

Example 2 in the *Specification* (¶¶ [0059]-[0064]) further shows that the rate of high temperature oxidation of electropolished samples of a ferritic stainless steel having a composition that falls within the recited compositional ranges was significantly lower than that of otherwise identical non-electropolished samples. Figures 7 and 8, reproduced below, show that the electropolished samples oxidized at a substantially lower rate than the non-electropolished samples, including a mechanically polished sample.



These tests indicate that electropolishing ferritic stainless steels having a composition that falls within the compositional ranges recited in the claims electrochemically modifies the surfaces of these steels, and that the electrochemical modification uniquely reduces the high temperature oxidation of the steels. *Specification*, ¶ [0063]. These tests also indicate that mechanically polishing an



equivalent sample to a specular surface finish equal to that achieved with electropolishing does not result in the development of the distinctive aluminum-rich oxide scale and high temperature oxidation resistance. *Id.* Moreover, the test results presented in the Specification show that mechanically polishing a sample that has been electropolished reverses the electrochemical modification, thereby preventing the development of the distinctive aluminum-rich oxide scale and eliminating the significantly improved high temperature oxidation resistance achieved by the presently claimed invention. *Id.*

Example 3 in the Specification (¶¶ [0065]-[0068]) presents X-ray diffractometry analysis of the distinctive golden colored oxide scale that develops on electropolished ferritic stainless steels having a composition that falls within the compositional ranges recited in the claims. The analysis shows that the distinctive golden-colored oxide scale is aluminum-rich; comprises aluminum, chromium, and iron; and is of a single phase having a hematite structure. *Id.* at ¶ [0067]-[0068]. The hematite structure is shown to be different than that of  $\text{Fe}_2\text{O}_3$ , alpha  $\text{Cr}_2\text{O}_3$ , and alpha  $\text{Al}_2\text{O}_3$ . The measured lattice parameters of the distinctive aluminum-rich oxide scale are different than that of  $\text{Fe}_2\text{O}_3$ , alpha  $\text{Cr}_2\text{O}_3$ , and alpha  $\text{Al}_2\text{O}_3$ . *Id.* The development of this distinctive aluminum-rich oxide scale was unexpected and surprising because there is no disclosure in the prior art that teaches or suggests the development of such a scale due to electropolishing.

Example 4 in the Specification (¶¶ [0069]-[0073]) shows that certain ferritic stainless steel chemistries are critical to the formation of the distinctive aluminum-rich oxide scale and the unexpected and significant improvement in oxidation resistance. In paragraph [0071] for example, it is shown that 0.2 to 1.0 weight percent aluminum is required for the development of the distinctive aluminum-rich oxide scale and the unexpected and significant improvement in oxidation resistance. In paragraph [0072] for example, it is shown that 0.02 to 1.0 weight percent total rare earth metal is required for the development of the distinctive aluminum-rich oxide scale and the unexpected and significant improvement in oxidation resistance. Thus, it has been shown that 0.2

to 1.0 weight percent aluminum and 0.02 to 1.0 weight percent total rare earth metal are necessary to achieve the unexpected improvement in oxidation resistance without sacrificing electrical conductivity or resulting in over-oxidation.

The features shown in the Specification as correlating with the unexpected and surprising development of the distinctive aluminum-rich oxide scale and the significant improvement in oxidation resistance are all recited in the claims of the Subject Application. These features and the unexpected results are confirmed by the uncontroverted expert testimony of Michael P. Brady, Ph.D, discussed below. Moreover, none of the cited references teach or suggest any of these features and significant results. Thus, based on a preponderance of the evidence, the claims of the Subject Application would not have been obvious, are clearly patentable, and should be allowed.

**5. Declaration of Michael P. Brady, Ph.D. under 37 C.F.R. § 1.132.**

Appellant respectfully submits that the Examiner has improperly ignored the expert testimony of Michael P. Brady, Ph.D., submitted via declaration on August 23, 2007, which is evidence that the distinctive aluminum-rich oxide scale and the significant improvement in high temperature oxidation resistance recited in the claims of the Subject Application would, in fact, have been unexpected before the Subject Application.

Michael P. Brady, Ph.D., is a senior researcher at the Oak Ridge National Laboratory, Oak Ridge, Tennessee. As discussed in the Declaration, Dr. Brady has substantial experience in the area of oxidation of stainless steels and other alloys, has evaluated and developed ferritic stainless steels and related alloys for use in solid oxide fuel cells, and is experienced with electropolishing and other surface preparation techniques. In the Declaration, Dr. Brady testifies that prior to the filing date of the Subject Application metallurgists did not believe that the high temperature oxidation resistance of ferritic stainless steels would be improved by electropolishing.

Nevertheless, the Examiner asserts that Dr. Brady's expert testimony is unpersuasive because the Declaration fails to set forth evidence to substantiate the allegedly conclusory statements contained in the testimony. This basis for discounting the declaratory evidence is improper and cannot be maintained.

In paragraph 9 of the Declaration, Dr. Brady testifies to the following:

At a time just prior to September 3, 2003, metallurgists conventionally believed that the high temperature oxidation resistance of a ferritic stainless steel surface would not be improved by electropolishing (flattening) the surface. Instead, metallurgists conventionally believed that mechanically deforming (roughening) the surface of a stainless steel would generally improve oxidation resistance by allowing a greater concentration of chromium in the steel access to the surface, to form a protective scale on the surface. It was believed that because electropolishing flattened the steel's surface and thereby reduced surface roughness, access of chromium to the surface would be inhibited, and this would inhibit growth of the chromium-rich scale necessary to prevent oxidation. Confirmation of the conventional beliefs regarding surface roughness and oxidation resistance in alloys generally is provided in the following references: C. S. Giggins et al., "The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900°C and 1000°C", 245 Transactions of the Metallurgical Society of AIME at 2509-2514 (December 1969); and J. M. Rakowski et al., "The Effect of Surface Preparation on the Oxidation Behavior of Gamma TiAl-Base Intermetallic Alloys", 35 Scripta Materialia at 1417-1422 (1996). Both of these references suggest the advantage of a mechanically deformed surface in regards to oxidation resistance.

Accordingly, in addition to providing his own expert opinion on the subject, Dr. Brady references scientific journals in his testimony confirming that persons having ordinary skill in the metallurgical arts believed that roughening the surface of metallic alloys, and not flattening the surface, would improve oxidation resistance. Applicant also discussed this conventional belief in detail in the Response to Office Action filed on August 23, 2007.

The present record lacks any evidence whatsoever that would support a prior recognition or suggestion in the art that the oxidation resistance of ferritic stainless steels having the composition recited in the claims of the Subject Application or, for that matter, any other ferritic stainless steel, would be improved by electropolishing. Thus, with reference to the evidence in the references cited in the Declaration, Dr. Brady has

found the results reported in the Subject Application for electropolished ferritic stainless steel to be unexpected and surprising, as would any ordinarily skilled person in the metallurgical arts.

Appellant maintains that compelling evidence of unexpected results is included in the Subject Application and was confirmed by Dr. Brady's testimony. Appellant further maintains that the statements presented by Dr. Brady in the Declaration are not conclusory, but rather are uncontroverted expert testimony. The Examiner has identified no basis for discounting or rebutting Dr. Brady's testimony, and Dr. Brady has submitted additional documentary evidence with his declaration, supporting his statements. Moreover, contrary to the Examiner's assertions, the subject matter recited in the claims of the Subject Application and the evidence of unexpected results provided in the Subject Application are commensurate in scope. The unexpected results and non-obviousness of the claims are supported by Dr. Brady's uncontroverted expert testimony.

The Examiner further argues that "... just because Michael P. Brady, Ph.D. finds the oxidation test results surprising does not necessarily mean that these results were not expected in the prior art, as set forth by the Examiner." *Advisory Action* issued January 28, 2010, p.6. Therefore, the Examiner concludes that the Declaration is not persuasive. The Examiner is incorrect for at least the following reasons.

First, the expert testimony provided in the declaration is independent evidence that is entitled to appropriate weight. See MPEP § 716.01(c)(III).

Second, the Examiner's argument that the testimony itself is unpersuasive is an improper argument because the determination of patentability must be made based on the evidence as a whole, not on the ability of each argument and piece of evidence to knock down any alleged *prima facie* case. *In re Piasecki*, 745 F.2d 1468, 1472, 223 USPQ 785, 788 (Fed. Cir. 1984); MPEP § 716.01(d). The ultimate determination of patentability must be based on consideration of the entire record, by a preponderance of evidence, with due consideration to the persuasiveness of any

arguments and any additional evidence, including testimonial evidence. *In re Oetiker*, 977 F.2d 1443. Facts established by rebuttal evidence must be evaluated along with the facts on which the conclusion of a *prima facie* case was reached, not against the conclusion itself. *In re Eli Lilly*, 902 F.2d 943, 14 USPQ2d 1741 (Fed. Cir. 1990).

Here, the Examiner completely disregards the facts established by Dr. Brady's testimony, namely, what a person skilled in the art would have understood and believed at the time of the invention claimed in the Subject Application. Dr. Brady is a qualified expert in the pertinent art and possesses at least an ordinary level of skill in the art. Accordingly, the Examiner cannot merely disregard Dr. Brady's expert testimony. In fact, in order to establish a *prima facie* case of obviousness, the burden is on the Examiner to provide controverting evidence that refutes or otherwise discounts Dr. Brady's expert testimony. Otherwise, any argument countering Dr. Brady's uncontroverted expert testimony would be improperly based on speculation and conjecture.

As discussed above in detail, the prior art does not teach or suggest the distinctive aluminum-rich oxide scale and the significant improvement in high temperature oxidation resistance recited in the claims of the Subject Application. Dr. Brady has testified that these features were unexpected and surprising at the time of the invention claimed in the Subject Application. The Examiner has not provided any evidence that controverts Dr. Brady's expert testimony as to what a person skilled in the art would have understood, believed, and expected at the time of the invention claimed in the Subject Application. Therefore, because Dr. Brady finds the results presented in Specification and claimed in the Subject Application surprising, and because the results are not taught or suggested in the prior art, it must be the case that the results were unexpected from the prior art set forth by the Examiner.

Furthermore, in addition to providing his own expert opinion on the subject, Dr. Brady refers to scientific journal articles in his declaration confirming that persons having ordinary skill in the metallurgical arts believed that roughening the

surface of metallic alloys, and not flattening the surface, would improve oxidation resistance.<sup>7</sup> Dr. Brady also confirms that electropolishing is a flattening technique.

The Examiner notes that the references cited by Dr. Brady in the Declaration relate to nickel and titanium alloys, whereas the alloys recited in the claims of the Subject Application are ferritic stainless steels. Therefore, the Examiner argues that it has not been established why people in the metallurgical arts believed that roughening the surface of a stainless steel, and not flattening the surface, would improve oxidation resistance. However, it is Dr. Brady's expert testimony that the conventional belief regarding oxidation resistance was generally applicable to metallic alloys, including nickel-base, titanium-base, and iron-base alloys. The Examiner cannot substitute his or her own opinion as to what is analogous art when a qualified expert in the pertinent art that possesses at least an ordinary level of skill in the art has testified as to the general understanding in the art at the time of the invention. Again, the burden is on the Examiner to provide controverting evidence that refutes or otherwise discounts Dr. Brady's expert testimony.

Appellant maintains that persuasive evidence of unexpected results is included in the Subject Application and is confirmed by Dr. Brady's testimony. Appellant further maintains that Dr. Brady's testimony is not conclusory, but rather is independent expert testimony, corroborated by independent analogous art. The Examiner has identified no basis for discounting or rebutting Dr. Brady's testimony, and Dr. Brady has cited additional documentary evidence with his declaration supporting his statements. Moreover, the subject matter recited in the claims of the Subject Application is

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<sup>7</sup> The following references are cited in the Declaration are of record in the Subject Application and provided in the *Evidence Appendix, infra*:

C. S. Giggins et al., "The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900°C and 1000°C," 245 *Transactions of the Metallurgical Society of AIME* (December 1969), pp. 2509-2514; and

J. M. Rakowski et al., "The Effect of Surface Preparation on the Oxidation Behavior of Gamma TiAl-Base Intermetallic Alloys," 35 *Scripta Materialia* (1996), pp. 1417-1422.

commensurate in scope with the evidence of unexpected results provided in the Specification.

Therefore, Appellant respectfully submits that the evidence of surprising and unexpected results, combined with the deficiencies of the cited prior art, weigh determinatively in favor of a legal conclusion of non-obviousness based on a preponderance of the evidence.

\* \* \* \*

Thus, in view of the forgoing discussion, Appellant respectfully submits that claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 are all patentable over the cited references and comply with all requirements under 35 U.S.C. § 112.

## VIII. CLAIMS APPENDIX

1. A method for making a ferritic stainless steel article having an oxidation resistant surface, the method comprising:

providing a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent; and

electropolishing at least one exposed surface of the ferritic stainless steel,

so that, when subjected to an oxidizing atmosphere at high temperature, the exposed electropolished surface develops an electrically conductive, aluminum-rich, oxidation resistant oxide scale comprising chromium and iron and having a hematite structure differing from  $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-Cr}_2\text{O}_3$ , and  $\alpha\text{-Al}_2\text{O}_3$ .

2. The method of claim 1, wherein lattice parameters  $a_0$  and  $c_0$  of the oxide scale differ from  $a_0$  and  $c_0$  of  $\text{Fe}_2\text{O}_3$ ,  $\alpha\text{-Cr}_2\text{O}_3$ , and  $\alpha\text{-Al}_2\text{O}_3$ .

3. The method of claim 1, wherein the at least one exposed electropolished surface develops the oxide scale when heated in an oxidizing atmosphere at a temperature in the range of 750°C to 850°C.

4. The method of claim 1, wherein the at least one exposed electropolished surface develops the oxide scale when heated in an oxidizing atmosphere for at least 100 hours at a temperature in the range of 750°C to 850°C.



5. The method of claim 1, wherein the oxide scale is characterized by lattice parameters  $a_o$  in the range of 4.95 to 5.04 Å and  $c_o$  in the range of 13.58 to 13.75 Å.

9. The method of claim 1, wherein the exposed electropolished surface develops the oxide scale when heated in an oxidizing atmosphere for at least 100 hours at a temperature in the range of 750°C to 850°C, and wherein the oxide scale is characterized by  $a_o$  in the range of 4.95 to 5.04 Å and  $c_o$  in the range of 13.58 to 13.75 Å.

10. A method for making a ferritic stainless steel article having at least one oxidation resistant surface, the method comprising:

providing a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent; and

electropolishing at least one exposed surface of the ferritic stainless steel, so that the exposed electropolished surface develops an aluminum-rich oxide scale when heated in an oxidizing atmosphere for at least 100 hours at a temperature in the range of 750°C to 850°C, the oxide scale comprising iron and chromium and having a hematite structure,  $a_o$  in the range of 4.95 to 5.04 Å, and  $c_o$  in the range of 13.58 to 13.75 Å.

11. A method for making a ferritic stainless steel article having an uncoated electropolished oxidation resistant surface, the method comprising:

providing a ferritic stainless steel comprising 0.2 to 1.0 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent; and  
electropolishing at least one exposed surface of the ferritic stainless steel.

13. The method of claim 11, wherein the at least one exposed electropolished surface develops an aluminum-rich oxide scale comprising iron and chromium and having a hematite structure,  $a_0$  in the range of 4.95 to 5.04 Å, and  $c_0$  in the range of 13.58 to 13.75 Å, when heated in an oxidizing atmosphere for at least 100 hours at a temperature in the range of 750°C to 850°C.

16. The method of claim 11, wherein the ferritic stainless steel comprises 0.4 up to 0.8 weight percent aluminum.

18. The method of claim 11, wherein the ferritic stainless steel comprises at least one metal selected from the rare earth metals cerium, lanthanum, and yttrium, and the transition metal hafnium.

20. The method of claim 11, wherein the ferritic stainless steel comprises, in weight percent, 18 up to 22 chromium, 0.4 to 0.8 aluminum, and 0.02 to 0.2 rare earth metal.

21. The method of claim 11, wherein the ferritic stainless steel further comprises, in weight percent, up to 3 nickel, up to 3 manganese, up to 0.7 silicon, up to 0.07 nitrogen, up to 0.07 carbon, and up to 0.5 titanium.

22. The method of claim 11, wherein the ferritic stainless steel comprises, in weight percent, about 22 chromium, about 0.6 aluminum, cerium, and lanthanum, wherein the sum of the weights of cerium and lanthanum is up to about 0.10.

25. The method of claim 11, wherein electropolishing the at least one exposed surface of the ferritic stainless steel comprises:

placing the at least one exposed surface of the ferritic stainless steel in a bath containing an electropolishing solution and a cathode; and

passing a current between the ferritic stainless steel and the cathode so that material is removed from the at least one exposed surface of the ferritic stainless steel, thereby reducing surface roughness of the at least one exposed surface.

26. The method of claim 11, wherein electropolishing the at least one exposed surface improves resistance of the at least one exposed surface to oxidation when subjected to a temperature and an atmosphere characteristic of operating conditions within a solid oxide fuel cell.

99. A method for making a ferritic stainless steel article having at least one oxidation resistant surface, the method comprising:

electropolishing at least one exposed surface of a ferritic stainless steel comprising 0.4 to 0.8 weight percent aluminum, 18 to 22 weight percent chromium, and 0.02 to 0.2 weight percent rare earth metals, wherein the rare earth metals are selected from the group consisting of cerium, lanthanum, praseodymium, and combinations of any thereof;

wherein the electropolishing chemically modifies the at least one exposed surface of the ferritic stainless steel so that the electropolished exposed surface develops an aluminum-rich oxide scale when heated in an oxidizing atmosphere at a temperature in the range of 750°C to 850°C, aluminum-rich the oxide scale comprising iron and chromium and having a hematite structure,  $a_o$  in the range of 4.95 to 5.04 Å, and  $c_o$  in the range of 13.58 to 13.75 Å.

100. The method of claim 99, further comprising heating the at least one exposed surface of the ferritic stainless steel article in an oxidizing atmosphere at a temperature in the range of 750°C to 850°C, wherein the exposed electropolished surface develops an aluminum-rich oxide scale comprising iron and chromium and having a hematite structure,  $a_o$  in the range of 4.95 to 5.04 Å, and  $c_o$  in the range of 13.58 to 13.75 Å.

101. The method of claim 99, wherein the electropolishing decreases the rate of oxidation of the ferritic stainless steel by at least one order of magnitude when compared to a non-electropolished sample of the same ferritic stainless steel, when heated in an oxidizing atmosphere at a temperature in the range of 750°C to 850°C.

## IX. EVIDENCE APPENDIX

The content of the Evidence Appendix includes the following:

- The Declaration of Michael P. Brady, Ph.D., submitted August 23, 2007;
- ASM Materials Engineering Dictionary, Fifth Printing, J. R. Davis ed., ASM International (2006), pp. 139 and 141;
- *Metallographic Practices for Wrought Stainless Steels* in ASM Specialty Handbook® of Stainless Steels, J. R. Davis ed., ASM International (1994), pp. 440-444;
- C. S. Giggins et al., "The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900°C and 1000°C," 245 *Transactions of the Metallurgical Society of AIME* (December 1969), pp. 2509-2514; and
- J. M. Rakowski et al., "The Effect of Surface Preparation on the Oxidation Behavior of Gamma TiAl-Base Intermetallic Alloys," 35 *Scripta Materialia* (1996), pp. 1417-1422.

**X. RELATED PROCEEDINGS APPENDIX**

The content of the Related Proceedings Appendix includes the following:

- None

**XI. CONCLUSION**

For the reasons discussed above, Appellant respectfully asks the Board to reverse the Examiner's rejections of claims 1-5, 9-11, 13, 16, 18, 20-22, 25, 26, and 99-101 under 35 U.S.C. § 103(a) and/or §112, as the case may be.

Respectfully submitted,

August 26, 2010  
Date

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of Rakowski

Application Serial No. 10/654,203

Filing Date: September 3, 2003

Art Unit 1793

Examiner Jesse R. Roe

Confirmation No. 5809

OXIDATION RESISTANT FERRITIC  
STAINLESS STEELS

Attorney Docket No. RL-2000

**APPEAL BRIEF – PART 2 of 2**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of Rakowski	:	
	:	OXIDATION RESISTANT FERRITIC
Group Art Unit 1742	:	STAINLESS STEELS
	:	
Serial No. 10/654,203	:	
	:	Confirmation No. 5809
Filed September 3, 2003	:	
	:	
Examiner Jessee Roe	:	

DECLARATION OF MICHAEL P. BRADY

Pittsburgh, Pennsylvania 15222-2312  
August 23, 2007

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

1. I, Michael P. Brady, declare as follows:
2. I am a citizen of the United States and currently reside at 110 Clemson Drive, Oak Ridge, TN 37830.
3. I am over the age of eighteen and am competent to make the statements in this Declaration.
4. I received a Ph.D. degree in Materials Science and Engineering from the University of Florida in August , 1993.
5. During 1993-1997, I was a National Research Council Postdoctoral Fellow at NASA's Glenn Research Center in the Environmental Durability Branch of the Materials Division and pursued research in high temperature alloy design and oxidation. In 1997, I joined the Materials Science and Technology Division at Oak Ridge National Laboratory as an ORISE Postdoctoral Fellow. I became a full time R&D staff member

at ORNL in 1998, and was promoted to Senior R&D staff in 2004. I am currently pursuing research in the development of corrosion-resistant, high temperature materials for cleaner and more efficient energy conversion and combustion systems, and the use of corrosion reactions to synthesize functional services for improved energy-related electrochemical systems and devices such as fuel cells. In fiscal year 2007, I am the lead/co-principle investigator for over \$3 million of research activities.

6. I am the author/coauthor of 5 issued U.S. Patents, 8 Pending U.S. Patents or ORNL Invention Disclosures, and over 80 publications in the areas of oxidation, alloy design, fuel cells, and coatings. Approximately half of my patents/invention disclosures are in the area of stainless steels, with 3 specifically directed to fuel cell issues. I am the author/coauthor of more than 15 archival journal articles specifically in the areas of stainless steels or fuel cells, including a recent paper on alumina-forming stainless steels in the international multidisciplinary journal *Science*, as well as specialty publications in leading metallurgical journals such as *Oxidation of Metals*, *Scripta Materialia*, *Journal of Power Sources*, *Metallurgical and Materials Transactions*, and *International Journal of Hydrogen Energy*. I also serve on the international advisory board of the journal *Oxidation of Metals*, and act as a technical reviewer for virtually every major metallurgical related journal.

7. I have specifically led efforts devoted to the evaluation and development of ferritic stainless steels (and related alloys) for SOFC fuel cells. I have conducted oxidation studies of ferritic stainless steels, as well as austenitic, Ni-base, Cr-base, and intermetallic alloys. I am well versed in surface preparation methods, including mechanical abrasion and electropolishing.

8. I have thoroughly reviewed U.S. Patent Application Serial No. 10/654,203 to Rakowski (the "Rakowski application"). The Rakowski application describes a method of electrochemically modifying a surface of a ferritic stainless steel to improve the oxidation resistance of the surface when exposed to high temperature, oxidizing environments, such as the environment within a solid oxide fuel cell ("SOFC"). Electropolishing is a well known method of electrochemically modifying a steel surface and operates by removing material from the surface to flatten (smooth) the surface. A

benefit of electropolishing is that the smoothed surface better reflects light and, therefore, the appearance of the surface is improved. It can also be used to minimize surface defects to improve other properties such as fatigue resistance. I am not aware of any previous findings of electropolishing enhancing high temperature oxidation resistance.

9. At a time just prior to September 3, 2003, metallurgists conventionally believed that the high temperature oxidation resistance of a ferritic stainless steel surface, as well as other classes of high temperature alloys, would not be improved by electropolishing the surface. Instead, metallurgists conventionally believed that mechanically deforming (roughening) the surface of a stainless steel would introduce cold work and dislocations, resulting in a fine local surface grain size on heating to high temperatures, that would generally improve oxidation resistance by increasing outward diffusion of the protective scale forming element (typically Cr or Al). It was believed that highly polished surfaces, either by mechanical polishing or electropolishing, result in a low defect surface microstructure, which does not recrystallize to a fine local grain size and therefore does not provide preferential outward diffusion paths to enhance protective oxide scale formation. It is general practice in the oxidation research community to perform oxidation tests with mechanically abraded surfaces, typically in the 600 grit surface finish range. The conventional beliefs regarding surface roughness, grain size refinement, and oxidation resistance in alloys have been prevalent for decades, for example refer to the references C. S. Giggins et al., "The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900°C and 1000°C", 245 Transactions of the Metallurgical Society of AIME at 2509-2514 (December 1969); and J. M. Rakowski et al., "The Effect of Surface Preparation on the Oxidation Behavior of Gamma TiAl-Base Intermetallic Alloys", 35 Scripta Materialia at 1417-1422 (1996). Both of these references suggest the advantage of a mechanically deformed surface in regards to establishing the desired continuous, protective oxide surface scale (chromia or alumina) to enhance oxidation resistance.

10. In light of the conventional beliefs regarding electropolishing discussed in paragraph 9 above, I was very surprised by the unexpected oxidation test results

described in the Rakowski application. The Rakowski application describes testing wherein the oxidation resistance of certain ferritic stainless steels was significantly improved by electropolishing surfaces of the steel, and also was improved relative to samples of the steel processed to have relatively rough surfaces. I believe that the results described in Rakowski were entirely unexpected prior to September 3, 2003, and were directly opposite to what a metallurgist would have predicted at that time based on the conventional beliefs in the field, described in paragraph 9 above. At a time just prior to September 3, 2003, metallurgists would have predicted that ferritic stainless steel surfaces that were electropolished would exhibit no beneficial oxidation-related effects, and likely a reduced level of oxidation resistance.

11. I believe that the results described in the Rakowski application are significant in that the inventor discovered that electropolishing provides a ready technique for further enhancing the oxidation resistance of surfaces of certain ferritic stainless steels.

12. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or document or any registration resulting therefrom.

Date: 8/23/07

Michael P Brady

*Am P. n*

# ASM MATERIALS ENGINEERING DICTIONARY

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J.R. Davis  
Davis & Associates



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Information Society

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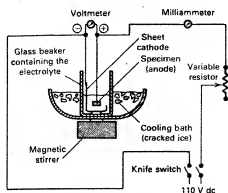
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FIG. 151



Basic laboratory setup for electropolishing and electrolytic etching

of an applied potential and a suitable electrolyte to produce the shapes and dimensions desired.

**electrolytic pickling.** *Pickling* in which electric current is used, the work being one of the electrodes.

**electrolytic polishing.** An electrochemical polishing process in which the metal to be polished is made the *anode* in an electrolytic cell where preferential dissolution at high points in the surface topography produces a specularly reflective surface (Fig. 151). Also referred to as *electropolishing*.

**electrolytic powder.** Powder produced by electrolytic deposition or by pulverizing of an electrodeposit.

**electrolytic protection.** See preferred term *cathodic protection*.

**electrolytic tough pitch.** A term describing the method of raw copper preparation to ensure a good physical- and electrical-grade copper-finished product.

**electromagnetic focusing device.** See *focusing device*.

**electromagnetic forming.** A process for forming metal by the direct application of an intense, transient magnetic field. The workpiece is formed without mechanical con-

tact by the passage of a pulse of electric current through a forming coil (Fig. 152). Also known as magnetic pulse forming.

**electromagnetic interference.** Interference related to accumulated electrostatic charge in a nonconductor.

**electromagnetic lens.** An electromagnet designed to produce a suitably shaped magnetic field for the focusing and deflection of electrons or other charged particles in electron-optical instrumentation.

**electromagnetic radiation.** Energy propagated at the speed of light by an electromagnetic field. The electromagnetic spectrum includes the following approximate wavelength regions:

Region	Wavelength, Å (metric)
Gamma-ray	0.005 to 1.40 (0.0005 to 0.14 nm)
X-ray	0.1 to 100 (0.01 to 10 nm)
Far-ultraviolet	100 to 2000 (10 to 200 nm)
Near-ultraviolet	2000 to 3800 (200 to 380 nm)
Visible	3800 to 7800 (380 to 780 nm)
Near-infrared	7800 to 30 000 (0.78 to 3 μm)
Middle-infrared	$3 \times 10^4$ to $3 \times 10^5$ (3 to 30 μm)
Far-infrared	$3 \times 10^5$ to $3 \times 10^6$ (30 to 300 μm)
Microwave	$3 \times 10^6$ to $1 \times 10^{10}$ (0.3 mm to 1 m)

**electromagnetism.** Magnetism caused by the flow of an electric current.

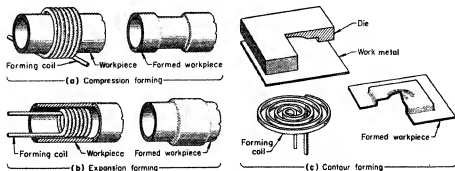
**electromechanical polishing.** An attack-polishing method in which the chemical action of the polishing fluid is enhanced or controlled by the application of an electric current between the specimen and the polishing wheel.

**electrometallurgy.** Industrial recovery or processing of metals and alloys by electric or electrolytic methods.

**electrometric titration.** A family of techniques in which the location of the endpoint of a *titration* involves the measurement of, or observation of changes in, some electrical quantity. Examples of such quantities include potential, current, conductance, frequency, and phase.

**electromotive force.** (1) The force that determines the flow

FIG. 152



Three basic methods of electromagnetic forming



**electron beam welding.** A welding process that produces coalescence of metals with the heat obtained from a concentrated beam composed primarily of high-velocity electrons impinging upon the surfaces to be joined. Welding can be carried out at atmospheric pressure (non-vacuum), medium vacuum (approximately  $10^{-3}$  to 25 torr), or high vacuum (approximately  $10^{-6}$  to  $10^{-3}$  torr).

**electron compound.** An intermediate phase on a *phase diagram*, usually a binary phase, that has the same crystal structure and the same ratio of valence electrons to atoms as those of intermediate phases in several other systems. An electron compound is often a solid solution of variable composition and good metallic properties. Occasionally, an ordered arrangement of atoms is characteristic of the compound, in which case the range of composition is usually small. Phase stability depends essentially on electron concentration and crystal structure and has been observed at valence-electron-to-atom ratios of  $\frac{3}{2}$ ,  $\frac{2}{3}$ , and  $\frac{7}{4}$ .

**electron diffraction.** The phenomenon, or the technique of producing diffraction patterns through the incidence of electrons upon matter. See also *diffraction pattern*.

**electron energy loss spectroscopy (EELS).** A spectrographic technique in the electron microscope that analyzes the energy distribution of the electrons transmitted through the specimen. The energy loss spectrum is characteristic of the chemical composition of the region being sampled.

**electron flow.** A movement of electrons in an external circuit connecting an *anode* and *cathode* in a corrosion cell; the current flow is arbitrarily considered to be in an opposite direction to the electron flow.

**electron gun.** A device for producing and accelerating a beam of electrons.

**electronic ceramics.** See *Technical Brief 14*.

**electronic heat control.** A device for adjusting the heating value (rms value) of the current in making a resistance weld by controlling the ignition or firing of the electronic devices in an electronic contactor. The current is initiated each half-cycle at an adjustable time with respect to the zero point on the voltage wave.

**electronic packaging.** The technical discipline of designing a protective enclosure for an electronic circuit so that it will both survive and perform under a plurality of environmental conditions.

**electron image.** A representation of an object formed by a beam of electrons focused by an electron-optical system. See also *image*.

**electron lens.** A device for focusing an electron beam to produce an image of an object.

**electron micrograph.** A reproduction of an image formed by the action of an electron beam on a photographic emulsion.

**electron microscope.** An electron-optical device that produces a magnified image of an object. Detail may be

revealed by selective transmission, reflection, or emission of electrons by the object. See also *scanning electron microscope* and *transmission electron microscope*.

**electron microscope column.** The assembly of gun, lenses, specimen, and viewing and plate chambers. See also the figure accompanying the term *scanning electron microscope*.

**electron microscopy.** The study of materials by means of an electron microscope.

**electron microscopy impression.** See *impression*.

**electron multiplier phototube.** See *photomultiplier tube*.

**electron optical axis.** The path of an electron through an electron-optical system, along which it suffers no deflection due to lens fields. This axis does not necessarily coincide with the mechanical axis of the system.

**electron optical system.** A combination of parts capable of producing and controlling a beam of electrons to yield an image of an object.

**electron probe.** A narrow beam of electrons used to scan or illuminate an object or screen.

**electron probe x-ray microanalysis (EPMA).** A technique in analytical chemistry in which a finely focused beam of electrons is used to excite an x-ray spectrum characteristic of the elements in a small region of the sample. Compositional mapping determines elemental location and concentration (Fig. 154).

**electron scattering.** Any change in the direction of propagation or kinetic energy of an electron as a result of a collision.

**electron spin resonance (ESR) spectroscopy.** A form of spectroscopy similar to nuclear magnetic resonance, except that the species studied is an unpaired electron, not a magnetic nucleus.

**electron trajectory.** The path of an electron.

**electron velocity.** The rate of motion of an electron.

**electron wavelength.** The wavelength necessary to account for the deviation of electron rays in crystals by wave-diffraction theory. It is numerically equal to the quotient of *Planck's constant* divided by the electron momentum.

**electrophoresis.** Transport of charged colloidal or macromolecular materials in an electric field.

**electroplate.** The application of a metallic coating on a surface by means of electrolytic action.

**electroplating.** The electrodeposition of an adherent metallic coating on an object serving as a *cathode* for the purpose of securing a surface with properties or dimensions different from those of the basis metal.

**electropolishing.** A technique commonly used to prepare metallographic specimens, in which a high polish is produced making the specimen the *anode* in an *electrolytic cell*, where preferential dissolution at high points smooths the surface. Also referred to as *electrolytic polishing*.

# ASM Specialty Handbook<sup>®</sup>

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## Stainless Steels

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# Metallographic Practices for Wrought Stainless Steels

METALLOGRAPHIC PROCEDURES used to prepare wrought stainless steels for macroscopic and microscopic examination are similar to those used for carbon and alloy steels and for tool steels (see the articles "Carbon and Alloy Steels" and "Tool Steels" in Volume 9, *Metallography and Microstructures*, of the *ASM Handbook*). However, certain types require careful attention to prevent artifacts. Because the austenitic grades work-harden readily, cutting and grinding must be carefully executed to minimize deformation. The high-hardness martensitic grades that contain substantial undissolved chromium carbide are difficult to polish while fully retaining the carbides. The most difficult of such grades to prepare is type 440C, particularly in the annealed or annealed and quenched condition. For the most part, preparation of stainless steels is reasonably simple if the basic rules for metallographic preparation are followed. However, unlike carbon, alloy, and tool steels, etching techniques are more difficult due to the high corrosion resistance of stainless steels and the vari-

ous second phases that may be encountered. References 1 to 3 provide additional details on the metallography of stainless steels.

## Macroexamination

The procedures used to select and prepare stainless steel disks for macroetching are identical to those used for carbon, alloy, and tool steels. Because these grades are more difficult to etch, however, all surfaces to be etched must be smooth ground or polished. Saw-cut surfaces will yield little useful information if they are macroetched. The macroetching procedure is described in ASTM E 381 ("Standard Method of Macroetch Testing, Inspection, and Rating Steel Products, Comprising Bars, Billets, Blooms, and Forgings").

Macroetchants for stainless steels are listed in Table 1. Heated macroetchants are used with stainless steels in the same manner as carbon, alloy, or tool steels. Etchant compositions are often more complex and more aggressive. In the study of weld microstructures, it is quite common to polish the section and use one of the general-purpose microetchants.

The standard sulfur print technique (Ref 1) can be used to reveal the distribution of manganese sulfide (MnS) inclusions in stainless steels. However, if the manganese content of the grade is low, chromium will substitute for manganese in the sulfides, and the sulfur print intensity will decrease. As the manganese content decreases below approximately 0.60%, chromium substitutes for manganese. At manganese contents below approximately 0.20%, pure chromium sulfides will form. These produce no image in the sulfur print test.

Figure 1 shows the macrostructure of a 480 mm (19 in.) diameter forged bloom of type 406 stainless steel that was made from a 1 m (40 in.) diameter ingot (Ref 3). Due to its large size, the disk was quartered before macroetching with equal parts of hydrochloric acid (HCl) and water at 70 °C (160 °F). As might be expected, the grain structure is much finer at the surface than in the interior. Figure 2 shows the macrostructure of a continuously cast 125 mm (5 in.) square billet of type 430 stainless steel in the as-cast condition. The disk was macroetched in the same manner as the forged type 406 bloom, but it was given a subsequent brightening/desmutting etch in a heated solution (also 70 °C, or 160 °F) of six parts water,

five parts nitric acid (HNO<sub>3</sub>), and one part hydrofluoric acid (HF). The disk exhibits the classic pattern of very fine grains at the surface and columnar grains extending from this region to near the center, where the grains are equiaxed.

## Microexamination

Sectioning techniques for stainless steels are identical to those used for carbon, alloy, or tool steels. Grades softer than approximately 35 HRC can be cut using a band saw or power hacksaw. However, such cutting produces substantial deformation and should be avoided with the deformation-sensitive austenitic grades. Deformation will be greatly reduced if cutting is performed using abrasive cutoff wheels with the proper degree of bonding. Shearing can be used with the ferritic grades but should be avoided with the austenitics. See the article "Sectioning" in Volume 9 of the *ASM Handbook* for additional information.

Mounting procedures, when required, are identical to those used for carbon, alloy, and tool steels. If edge preservation is required for near-surface examination, compression-mounting epoxy can be used, or specimens can be plated with electroless nickel. For specimens with surface cracks, it may be useful to vacuum impregnate the

Table 1 Macroetchants for stainless steels

Etchant	Comments
1. 50 mL HCl, 10 g CuSO <sub>4</sub> (copper sulfate), 50 mL H <sub>2</sub> O(a)	Martell's reagent. General-purpose macroetch; can be heated
2. 50 mL HCl, 50 mL H <sub>2</sub> O, 20 mL 30% H <sub>2</sub> O <sub>2</sub>	Mix HCl and H <sub>2</sub> O, heat to 70-75 °C (160-170 °F). Immerse specimen and add H <sub>2</sub> O <sub>2</sub> in steps when foaming stops; do not mix, Lepin's No. 1 etch.
3. (a) 15 g (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (ammonium persulfate) and 75 mL H <sub>2</sub> O (b) 250 g FeCl <sub>3</sub> and 100 mL H <sub>2</sub> O (c) 30 mL HNO <sub>3</sub>	Combine (a) and (b), then add (c); immerse specimen at room temperature; use fresh
4. 1 part HCl and 1 part H <sub>2</sub> O	Standard hot etch. Use at 70-80 °C (160-180 °F), 15-45 min; desmut by dipping in warm 20% aqueous HNO <sub>3</sub> solution to produce a bright surface
5. 10-40 mL HNO <sub>3</sub> , 3-10 mL 48% HF, 25-50 mL H <sub>2</sub> O	Use at 70-80 °C (160-180 °F); immerse until the desired degree of contrast is obtained
6. 50 mL HCl and 25 mL saturated CuSO <sub>4</sub> in H <sub>2</sub> O	Use at 75 °C (170 °F); immerse until the desired degree of contrast is obtained

(a) When water is specified, use distilled water.

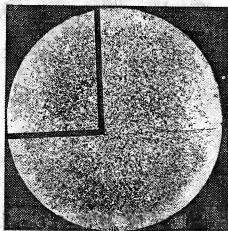


Fig. 1 Macrostructure of a 480 mm (19 in.) diam type 406 stainless steel forged bar produced from a 1 m (40 in.) diam ingot. Courtesy of C.F. Vander Voort, Carpenter Technology Corp.

**Table 2** Electropolishing procedures for stainless steels

Electrolyte composition	Comments
1. 50 mL HClO <sub>4</sub> (perchloric acid), 750 mL ethanol, 140 mL H <sub>2</sub> SO <sub>4</sub>	Add HClO <sub>4</sub> last, with care. Use at 20 V dc, 0.3-1.3 A/cm <sup>2</sup> (1.9-8.4 A/in. <sup>2</sup> ), 20 °C (70 °F), 20-60 s. Rinse immediately after polishing.
2. 78 mL HClO <sub>4</sub> , 90 mL H <sub>2</sub> O, 730 mL ethanol, 100 mL butyl cellosolve	Add HClO <sub>4</sub> last, with care. Use at 0.5-1.5 A/cm <sup>2</sup> (3.2-9.7 A/in. <sup>2</sup> ), 20 °C (70 °F) max.
3. 62 mL HClO <sub>4</sub> , 700 mL ethanol, 100 mL butyl cellosolve, 137 mL H <sub>2</sub> O	Add HClO <sub>4</sub> last, with care. Use at 1.2 A/cm <sup>2</sup> (7.7 A/in. <sup>2</sup> ), 20 °C (70 °F), 20-25 s.
4. 25 g CrO <sub>3</sub> , 133 mL acetic acid, 7 mL H <sub>2</sub> O	Use at 20 V dc, 0.09-0.22 A/cm <sup>2</sup> (0.58-1.4 A/in. <sup>2</sup> ), 17-19 °C (63-66 °F), 6 min. Dissolve CrO <sub>3</sub> in solution heated to 60-70 °C (140-160 °F).
5. 37 mL H <sub>3</sub> PO <sub>4</sub> , 56 mL glycerol, 7 mL H <sub>2</sub> O	Use at 0.78 A/cm <sup>2</sup> (5.0 A/in. <sup>2</sup> ) 100-120 °C (212-250 °F), 5-10 min.
6. 6 mL HClO <sub>4</sub> and 94 mL ethanol	Use at 35-40 V dc, 24 °C (75 °F), 15-60 s.

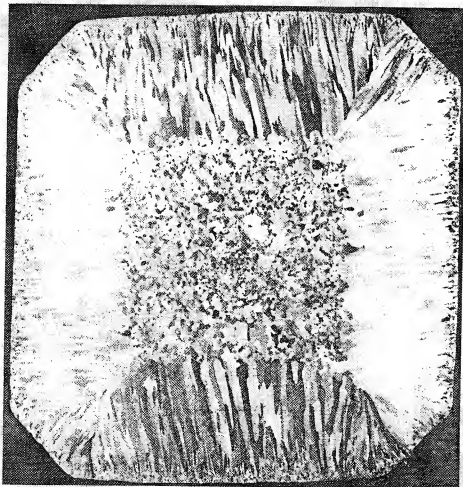
(a) When water is specified, use distilled water.

specimen in cold-setting epoxy; epoxy will be drawn into the cracks, minimizing bleedout problems after etching. See the article "Mounting of Specimens" in Volume 9 of the *ASM Handbook* for a complete discussion of mounting materials and problems associated with various mounting methods.

**Grinding** is performed using 120-, 240-, 320-, 400-, and then 600-grit water-cooled silicon carbide papers. Care must be taken, particularly when grinding austenitic grades, to remove the cold work from cutting and from each grinding step. In general, speeds of approximately 300 rpm and moderate, firm pressure are used. Grinding times are 1 to 2 min per step. If grinding is carried out by hand, the specimen should be rotated 45 to 90° between each step. Automatic grinding devices produce omnidirectional grinding patterns. See the article "Grinding, Abrasion, and Polishing" in Volume 9 of the *ASM Handbook* for additional information.

**Polishing.** After grinding, specimens are usually rough polished using 6- or 3- $\mu$ m diamond as a paste, spray, or slurry on napless, low-nap, or medium-nap cloths. Edge flatness and inclusion retention are usually improved by using napless cloths, although scratch removal may not be as complete as with medium-nap cloths. A lubricant extender compatible with the diamond abrasive should be used to moisten the cloth and reduce drag. A wheel speed of approximately 150 rpm is usually adequate. Pressure should be moderate and firm; specimen rocking should be avoided if polishing is carried out by hand.

For hand polishing, rotate the specimen around the wheel in the direction opposite to wheel rotation while moving from center to edge. Automatic devices generally produce better edge flatness than hand polishing. After this step, the

**Fig. 2** As-cast microstructure of a 125 mm (5 in.) square billet of continuously cast type 430 stainless steel. Courtesy of G.F. Vander Voort, Carpenter Technology Corp.

specimen may be polished using 1  $\mu$ m diamond abrasive on a medium-nap cloth. For routine examination, a 1  $\mu$ m diamond finish may be adequate, particularly for the hardenable grades.

To produce high-quality, scratch-free surfaces suitable for photomicroscopy, specimens should be final polished using one or more fine abrasives. The most commonly used final abrasives are 0.3  $\mu$ m  $\alpha$ -alumina ( $Al_2O_3$ ) or 0.05  $\mu$ m  $\gamma$ - $Al_2O_3$ . Medium-nap cloths are usually used. Polishing with these abrasives, using a polish mixed as a water slurry, is performed in the same manner as diamond polishing. Specimens should be carefully cleaned between each rough and final polishing step to avoid contamination at the next step. Colloidal silica is a highly suitable final abrasive for stainless steels.

Stainless steels, particularly the austenitic grades, are often polished electrolytically. In most cases, electropolishing is performed after grinding to a 600-grit silicon carbide finish. Table 2 lists recommended procedures. Electropolishing usually produces high-quality, deformation-free surfaces; however, inclusion attack is encountered, and second phases may be attacked preferentially.

**Etching.** For inclusion examination, etching is not required, although it is necessary for examining the microstructure. Although stainless steels are reasonably easy to polish, etching is generally a more difficult step. The corrosion resistance of stainless steels and the potential microstructural complexity of these alloys make selection of the best etchant a more difficult problem than for carbon and alloy steels.

Stainless steel etchant ingredients are dissolved in water, methanol, or ethanol; glycerol; or a mixture of these solvents. Reagents with alcohol or glycerol as the solvent provide better wetting of the surface than water-based reagents and generally provide more uniform etching. Because alcohol reduces dissociation, alcohol-based reagents can be made more concentrated without becoming too powerful for controlled etching. Stainless steel surfaces passivate; therefore, reducing conditions are preferred to oxidizing conditions that promote passivity. Consequently, stainless steel etchants often contain HCl, sulfuric acid ( $H_2SO_4$ ), or HF acid, although  $HNO_3$  may be used alone or mixed with HCl to produce aqua regia or a modified aqua regia. Swabbing, instead of immersion, may be desired to obtain more

uniform etch results. Electrolytic etching is also very popular, because it produces uniform etching, is easier to control, and gives reproducible results. Numerous etchants have been proposed for stainless steels; each has advantages and disadvantages.

Etching the 400-series ferritic or martensitic grades is simpler than the 200- or 300-series austenitics or the 600-series precipitation-hardenable grades. Vilella's reagent (4% picral + HCl) or superalloy is commonly used with ferritic and martensitic grades. Etching of the extra-low-interstitial-content ferritic grades to observe the grain boundaries, however, is much more difficult than with the ordinary ferritics. Microetchants are listed in Table 3.

Etching of the austenitic grades to examine the grain structure is difficult with most standard reagents. As shown in the photomicrographs in the article "Microstructures of Wrought Stainless Steels" in this Volume, most of the standard reagents reveal only some of the grain boundaries. Tint etching, which requires a high-quality polish for good results, reveals all of the grains by color contrast. To measure the grain size when a more accurate value is required than can be obtained by a comparison chart rating, all the boundaries must be revealed. Twin boundaries are ignored.

Sensitizing the specimen by heating it for 1 to 6 h at 650 °C (1200 °F) will facilitate observation of the grain boundaries. An alternate technique (Ref. 4, 5) involves electrolytically etching the solution-annealed specimen in 60% aqueous HNO<sub>3</sub> (see Table 3). With this procedure, twin boundaries are not revealed. This etch will also bring out prior-austenite grain boundaries in solution-annealed, but not aged, precipitation-hardened grades. For structure-property correlations, the mean lineal intercept value for grain and twin boundaries should be measured, because the twin boundaries also contribute to strengthening. Such a measurement should not be converted to a grain size value.

Various alkaline ferricyanide reagents, such as Murakami's reagent, have been widely used to etch austenitic stainless steels for phase identification. The colors produced by these etchants vary with etchant composition, temperature, time, and phase orientation. When using a particular reagent in the prescribed manner, the colors obtained may differ from those reported in the literature. However, the etch response, that is, what is attacked and what is not attacked, is highly reproducible.

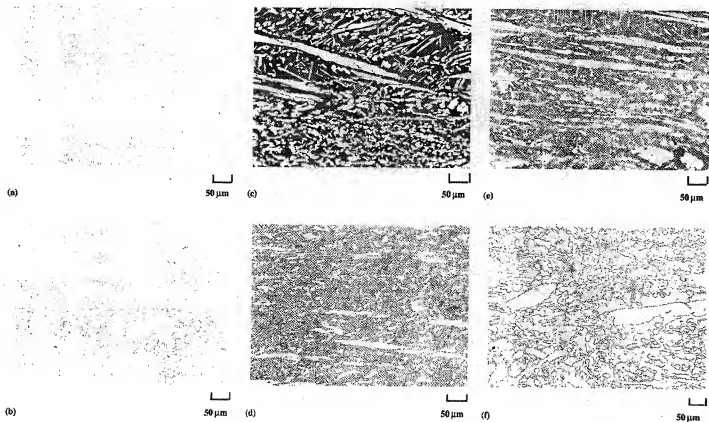
When using the standard formulation of Murakami's reagent at room temperature, for example, the carbides will be attacked in 7 to 15 s;  $\sigma$ -phase will be only lightly attacked after 3 min. If higher concentrations of potassium hydroxide (KOH) or sodium hydroxide (NaOH) and potassium ferricyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>) are used at room temperature,  $\sigma$ -phase will be attacked instead of the carbides. Used boiling, the standard formulation attacks ferrite, carbide, and  $\sigma$ -phase, although some evidence indicates that  $\sigma$ -phase will not be attacked. Therefore, when using this reagent or one of its numerous modifications, directions should be followed carefully. Ex-

Table 3 Microetchants for stainless steel

Etchants	Comments	Etchants	Comments
1. 1 g picric acid, 5 mL HCl, 100 mL ethanol	Vilella's reagent. Use at room temperature to 1 min. Outlines second-phase particles (carbides, $\sigma$ phase, $\delta$ ferrite), etches martensite	14. 10 g NaCN (sodium cyanide) and 100 mL H <sub>2</sub> O	Electrolytic etch at 6 V dc, 25-mm spacing. 5 min, platinum cathode. Sigma darkened, carbides light, ferrite outlined, austenite not attacked. Good for revealing carbides. Use with care under a hood.
2. 1.5 g CuCl <sub>2</sub> (cupric chloride), 33 mL HCl, 33 mL ethanol, 33 mL H <sub>2</sub> O	Kalling's No. 1 reagent for martensitic stainless steels. Use at room temperature. Martensite dark, ferrite colored, austenite not attacked	15. 10 mL HCl and 90 mL methanol	Electrolytic etch at 1.5 V dc, 20 °C (70 °F) to attack $\sigma$ phase. Use at 6 V dc for 3-5 s to reveal structure.
3. 5 g CuCl <sub>2</sub> , 100 mL HCl, 100 mL ethanol	Kalling's No. 2 reagent. Use at room temperature. Ferrite attacked rapidly, austenite slightly attacked, carbides not attacked	16. 60 mL HNO <sub>3</sub> and 40 mL H <sub>2</sub> O	Electrolytic etch to reveal austenite grain boundaries (but not twins) in austenitic grades. With stainless steel cathode, use at 1.1 V dc, 0.075-0.14 A/cm <sup>2</sup> (0.48-0.90 A/in. <sup>2</sup> ), 120 s. With platinum cathode, use at 0.4 V dc, 0.055-0.066 A/cm <sup>2</sup> (0.35-0.43 A/in. <sup>2</sup> ), 45 s. Will reveal prior-austenite grain boundaries in solution-treated (but not aged) martensitic precipitation-hardenable alloys
4. 5 g CuCl <sub>2</sub> , 40 mL HCl, 30 mL H <sub>2</sub> O, 25 mL ethanol	Pry's reagent. For martensitic and precipitation-hardenable grades. Use at room temperature.	17. 50 g NaOH and 100 mL H <sub>2</sub> O	Electrolytic etch at 2.6 V dc, 5-10 s to reveal $\sigma$ phase in austenitic grades
5. 4 g CuSO <sub>4</sub> , 20 mL HCl, 100 mL H <sub>2</sub> O	Marble's reagent. Used primarily with austenitic grades. Use at room temperature to 10 s. Attacks $\sigma$ phase	18. 56 mL KOH and 100 mL H <sub>2</sub> O	Electrolytic etch at 1.5-3 V dc for 3 s to reveal $\sigma$ phase (red-brown) and ferrite (bluish). Chi colored same as sigma
6. 3 parts glycerol, 2-5 parts HCl, 1 part HNO <sub>3</sub>	Glyceric. Popular etch for all stainless grades. Higher HCl content reduces pitting tendency. Use fresh, never store. Dacau when reagent is orange colored. Use with care under a hood. Add HNO <sub>3</sub> last. Immerse or swab a few seconds to a minute. Attacks $\sigma$ phase, outlines carbides. Substitution of water for glycerol increases attack rate	19. 20 g NaOH and 100 mL H <sub>2</sub> O	Electrolytic etch at 20 V dc, for 5-20 s to outline and color $\delta$ -ferrite twin
7. 45 mL HCl, 15 mL HNO <sub>3</sub> , 20 mL methanol	Methanolic aqua regia. Used with austenitic grades to reveal grain structure, outline ferrite and $\sigma$ phase	20. NH <sub>4</sub> OH (conc)	Electrolytic etch at 1.5-5 V dc for 10-60 s. Very selective. At 1.4 V, carbide completely etched in 40 s; sigma unaffected after 180 s. At 6 V, $\sigma$ phase etched after 40 s
8. 15 mL HCl, 5 mL HNO <sub>3</sub> , 100 mL H <sub>2</sub> O	Dilute aqua regia for austenitic grades. Uniform etching of austenite, outlines carbides, $\sigma$ phase, and ferrite (sometimes attacked)	21. 10 g (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and 100 mL H <sub>2</sub> O	Use at 6 V dc for 10 s to color carbide dark brown
9. 4 g KMnO <sub>4</sub> (potassium permanganate), 4 g NaOH, 100 mL H <sub>2</sub> O	Groesbeck's reagent. Use at 60-90 °C (140-195 °F) to 10 min. Colors carbides dark, $\sigma$ phase gray, ferrite and austenite not affected	22. 200 mL HCl and 1000 mL H <sub>2</sub> O	Beraha's tint etch for austenitic, duplex, and precipitation-hardenable grades. Add 0.5-1.0 g K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> per 100 mL of solution (if etching is too rapid, use a 10% aqueous HCl solution). Immerse at room temperature (never swab) for 30-120 s until surface is reddish
10. 30 g KMnO <sub>4</sub> , 30 g NaOH, 100 mL H <sub>2</sub> O	Modified Groesbeck's reagent. Use at 90-100 °C (195-212 °F) for 20 s to 10 min to color ferritic dark in duplex alloys. Austenite not affected		Austenite colored, carbides not colored. Longer immersion colors ferrite lightly. If coloration is inadequate, add 24 g NH <sub>4</sub> HF (ammonium bifluoride) to stock reagent at 10 min
11. 10 g K <sub>3</sub> Fe(CN) <sub>6</sub> , 10 g KOH or 7 g NaOH, 100 mL H <sub>2</sub> O	Murakami's reagent. Use at room temperature to 60 s to reveal carbides; $\sigma$ phase faintly revealed by etching to 3 min. Use at 80 °C (176 °F) to boiling to 60 min to darken carbides. Sigma may be colored blue, ferrite yellow to yellow-brown, austenite not attacked. Use under a hood.	23. 20 g picric acid and 100 mL HCl	Etch by immersion. Develops grain boundaries in austenitic and $\delta$ -ferrite in duplex alloys
12. 30 g KOH, 30 g K <sub>3</sub> Fe(CN) <sub>6</sub> , 100 mL H <sub>2</sub> O	Modified Murakami's reagent. Use at 95 °C (203 °F) for 5 s. Colors $\sigma$ phase reddish brown, ferrite dark gray, austenite unattacked, carbide black. Use under a hood.	24. Saturated aqueous Ba(OH) <sub>2</sub> (barium hydroxide)	Attacks carbides well before $\sigma$ phase in austenitic grades when used at 1.5 V dc, but attacks both equally when used at 3-6 V dc. Has been used to differentiate $\sigma$ phase and Laves phase (use at 4.3 V dc, platinum cathode, 20 s). Chi is stained mottled-purple. Laves is not colored. Ferrite is stained tan
13. 10 g malic acid and 100 mL H <sub>2</sub> O	Popular electrolytic etch, 6 V dc, 25-mm spacing. 15-30 s reveals carbides, grain boundaries revealed after 45-60 s or $\sigma$ phase outlined after 6 s. Lower voltages (1-3 V dc) can be used. Dissolves carbides. Sigma strongly attacked, austenite moderately attacked, ferrite not attacked	25. 50 mL each H <sub>2</sub> O, ethanol, methanol, and HCl plus 1 g CuCl <sub>2</sub> , 3.5 g FeCl <sub>3</sub> , 2.5 mL HNO <sub>3</sub>	Ralph's reagent. Use by swabbing. Can be stored. General purpose etch for most stainless steels. Does not attack sulfides in free-machining grades

(a) When water is specified, use distilled water





**Fig. 3** A comparison of various etchants to reveal the microstructure of 7-Mo PLUS duplex stainless steel (longitudinal plane). (a) Glyceregia chemical etch. (b) Ethanolic 15% HCl chemical etch. (c) Beraha's first etch to color the ferrite. (d) Electrolytic 20% NaOH to color the ferrite. (e) Electrolytic 56% KOH to color the ferrite. (f) Electrolytic 60% HNO<sub>3</sub>. All at 200 $\times$ . Courtesy of G.F. Vander Voort, Carpenter Technology Corp.

perimentation with specimens of known constitution is also recommended.

Electrolytic reagents, which are used often with austenitic and duplex grades, provide greater control of the etching process and are highly reproducible. Perhaps the most commonly used electrolytic reagent is 10% aqueous oxalic acid, which will reveal carbides after a short etch if they are present (see Table 3). When carbides are not present, the austenite grain boundaries will be revealed in 15 to 60 s. If ferrite is present, it will be outlined after 10 to 15 s.

Electrolytic reagents are generally quite simple in composition. The selectivity of electrolytic reagents based on various hydroxide solutions has been demonstrated (Ref 6). Strong hydroxide solutions attack  $\sigma$ -phase preferentially to carbides; weak hydroxide solutions attack carbides much more readily than  $\sigma$ -phase. Therefore, to reveal  $\sigma$ -phase, 10 N KOH is employed, and to reveal carbides, concentrated ammonium hydroxide (NH<sub>4</sub>OH) is used. For intermediate-strength hydroxide solutions, etching response is altered by a change in the applied potential.

Several sequential etching procedures have been suggested for phase identification in austenitic stainless steels. One procedure (Ref 6) involves etching first with Vilella's reagent to

outline the phases present. Next, the specimen is electrolytically etched with 10 N KOH at 3 V dc for 0.4 s to color  $\alpha$ -phase, if present, but not carbides. The specimen is then electrolytically etched with concentrated NH<sub>4</sub>OH at 6 V dc for 30 s to color any carbides present. Another procedure (Ref 7) also begins with Vilella's reagent to reveal the constituents. Next, Murakami's reagent is used at room temperature to stain the carbides present. Any  $\sigma$ -phase or  $\delta$ -ferrite present is unaffected. Finally, the specimen is electrolytically etched with aqueous chromium trioxide (CrO<sub>3</sub>), which will attack carbides and  $\sigma$ -phase, but not  $\delta$ -ferrite. Murakami's reagent does not attack carbides in titanium- or niobium-stabilized stainless steels. These carbides are attacked slowly in electrolytic CrO<sub>3</sub>.

Delta-ferrite in martensitic, austenitic, or precipitation-hardenable grades can be preferentially colored by electrolytic etching with 20% aqueous NaOH at 20 V dc for 5 to 20 s. This procedure outlines and uniformly colors tan  $\delta$ -ferrite. Although the color varies with orientation, 10 N KOH also colors  $\delta$ -ferrite.

Potentiostatic etching (Ref 1 and 8) is frequently used for selective etching of constituents in stainless steels. This technique is similar to electrolytic etching, except a third electrode is in-

cluded to monitor the etch potential, which is controlled using a potentiostat. This technique affords the greatest possible control over etching.

Heat tinting is a useful technique with austenitic stainless steels. Phase delineation is improved by first etching with a general-purpose reagent, such as Vilella's. The specimen is then heated in air at 500 to 700 °C (930 to 1290 °F); 650 °C (1200 °F) has been most commonly used with times to 20 min. Austenite is colored more readily than ferrite, and carbides resist coloration longest. After 20 min at 650 °C (1200 °F), austenite is blue-green,  $\sigma$ -phase is orange, ferrite is light cream, and carbides are uncolored.

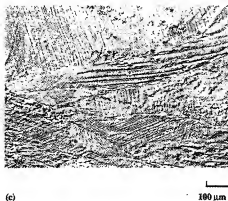
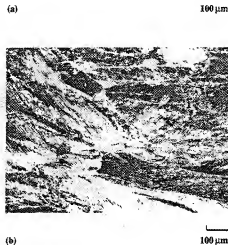
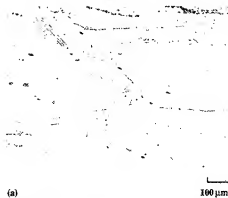
Magnetic colloids have also been used to detect ferromagnetic constituents in austenitic stainless steels. This technique, which is referred to as *magnetic etching*, has been extensively applied using a ferromagnetic colloid solution (Ferrolud) containing very fine magnetic particles (Ref 9). Delta-ferrite and strain-induced martensite are readily identified by this method. More detailed information on magnetic etching can be found in Volume 9 of the *ASM Handbook* (see Appendix 1 to the article "Etching").

Figure 3 illustrates the use of a variety of etchants to reveal the structure of a duplex stainless steel (UNS S32950, also known as Carpenter

**Table 4** Electropolishing procedures for preparing thin-foil stainless steel specimens

Solution composition	Comments
1. 3 or 10 mL HClO <sub>4</sub> and 95 or 90 mL acetic acid at 20 V dc	Popular electropolish for stainless steels. Used for window technique or for perforation of disk specimens. Keep solution cool.
2. (a) 10 mL HNO <sub>3</sub> and 90 mL H <sub>2</sub> O at 50 V dc (b) 10 mL HClO <sub>4</sub> , 20 mL glycerol, 70 mL ethanol at 65 V dc	Popular procedures for austenitic grades. Use (a) to electrodish specimens, then (b) for perforation.
3. 10 mL HClO <sub>4</sub> and 90 mL ethanol at 12 V dc, 0 °C (32 °F)	Popular electropolish for stainless steels. Use for perforation.
4. 40 mL H <sub>2</sub> SO <sub>4</sub> and 60 mL H <sub>2</sub> PO <sub>4</sub> at 35 V dc, 0.3 A/cm <sup>2</sup> (1.9 A/in. <sup>2</sup> )	Electropolish for stainless steels for perforation.
5. 25 g CrO <sub>3</sub> , 133 mL acetic acid, 7 mL H <sub>2</sub> O at 20 °C (70 °F)	Electropolish for stainless steels. Good for window method. Opacity of solution makes it difficult to use for jet perforation.
6. (a) 40 mL acetic acid, 30 mL H <sub>2</sub> PO <sub>4</sub> , 20 mL HNO <sub>3</sub> , 10 mL H <sub>2</sub> O at 80-120 V dc, 0.1 A/cm <sup>2</sup> (0.65 A/in. <sup>2</sup> ) (b) 54 mL H <sub>2</sub> PO <sub>4</sub> , 36 mL H <sub>2</sub> SO <sub>4</sub> , 10 mL ethanol at 6 V dc	Procedure for austenitic grades. Jet electrodish disks with (a) prior to final thinning with (b) to perforation.
7. 45 mL H <sub>2</sub> SO <sub>4</sub> , 30 mL H <sub>2</sub> SO <sub>4</sub> , 25 mL H <sub>2</sub> O at 6 V dc	Procedure for austenitic grades for perforation.

(a) When water is specified, use distilled water.

**Fig. 4** A comparison of various light microscope illumination modes to reveal the microstructure of a warm-worked high-manganese drill collar alloy (as-rolled) etched in acetic glycerol and viewed with (a) bright field illumination, (b) dark-field illumination, and (c) differential interference contrast illumination. All three photomicrographs show the same area. Courtesy of G.F. Vander Voort, Carpenter Technology Corp.

7-Mo PLUS). Table 3 should be consulted for procedure details.

**Illumination modes other than bright field** are of considerable value for examining stainless

steels (Ref 3). Oblique illumination or differential interference contrast (DIC) can be used to observe second-phase constituents more clearly, in the as-polished condition if there is a hardness difference, or after etching. The DIC illumination mode is also useful for examining grain structure, as is dark-field illumination. Polarized light has very limited use with stainless steels.

As an example of the use of various illumination modes, Fig. 4 demonstrates the superiority of dark-field illumination and DIC in revealing the structure of a high-manganese warm-worked drill collar austenitic stainless steel in the as-rolled condition. This figure shows that the bright field micrograph (Fig. 4a) is nearly featureless; however, the use of the dark-field mode (Fig. 4b) or DIC (Fig. 4c) reveals the deformed substructure clearly. Additional information on illumination modes associated with the light microscope can be found in the article "Optical Microscopy" in Volume 9 of the *ASM Handbook*.

**Electron Microscopy.** Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to examine the fine structure of stainless steels and for phase identification. Scanning electron microscopy examination uses the same specimens as optical (light) microscopy. As-polished specimens often can be examined, although etching is more common. Many second-phase constituents can be observed using backscattered elec-

tron detectors due to the adequate atomic number contrast between these phases and the matrix. However, secondary electron images produced from topographic contrast and atomic number contrast are most often used. Energy-dispersive x-ray analysis (EDXA) is prevalent for chemical analysis of second phases, although lightweight elements, such as carbon and nitrogen, cannot be detected unless thin-window or windowless EDXA detectors or wavelength-dispersive detectors are used. Detailed reviews of SEM, TEM, and EDXA can be found in Volumes 9, 10, and 12 of the *ASM Handbook*.

Transmission electron microscopy requires preparation of replicas or thin-foil specimens (see the article "Transmission Electron Microscopy" in Volume 9 of the *ASM Handbook*). Replicas may be made to reveal the outline and topography of the phases, or if the specimen is deeply etched, second-phase particles may be extracted. Extraction replicas permit analysis of second phases by electron diffraction and by EDXA. Thin-foil specimens can also be analyzed by these methods, although interference from the matrix is possible. Table 4 lists electropolishing procedures for producing stainless steel thin foils. Reference 10 is another excellent source of information on thin foil specimen preparation techniques for TEM examination.

**Bulk Extractions.** Although bulk samples can be directly analyzed by x-ray diffraction for phase identification, it is quite common to extract the second phases chemically and analyze the extracted particles. This eliminates the matrix and concentrates the second phase, facilitating identification of small amounts of the second-phase constituents. Bulk extraction of phases from wrought stainless steels is performed using electrolytes such as 10% HCl in methanol. Details concerning the use of such electrolytes are given in Ref 11 to 13.

## ACKNOWLEDGMENT

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# The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900° and 1100°C

C. S. Giggins and F. S. Pettit

*The oxidation properties of Ni-Cr alloys with fine grains, coarse grains, and deformed surface layers have been studied at temperatures of 900° and 1100°C in 0.1 atm of oxygen. The oxidation rates of alloys containing between 10 and 30 wt pct Cr have been found to be dependent upon the grain size of the alloy. Fine-grained alloys had smaller oxidation rates than coarse-grained alloys because of the selective oxidation of chromium at alloy grain boundaries. In this compositional range alloys with deformed surface layers behaved similar to fine-grained alloys due to recrystallization of the deformed surface layer.*

IN the preceding paper<sup>1</sup> it was found that during the oxidation of Ni-Cr alloys, the volume fraction of precipitated  $\text{Cr}_2\text{O}_3$  could be greater at alloy grain boundaries than at other areas of the alloy surface. In the case of alloys with chromium concentrations equal to or greater than 30 pct,<sup>2</sup> the volume fraction of  $\text{Cr}_2\text{O}_3$

<sup>1</sup>All compositions are given as weight percent unless specified otherwise.

precipitated at grain boundaries and within grains on the alloy surface both exceeded the critical amount required for lateral growth of the  $\text{Cr}_2\text{O}_3$  particles and the surfaces of these alloys were completely covered with a continuous, external layer of  $\text{Cr}_2\text{O}_3$  during oxidation. However, in the case of alloys with chromium concentrations between approximately 5 to 30 pct, the volume fraction of precipitated  $\text{Cr}_2\text{O}_3$  exceeded the critical value required for external scale formation only at grain boundaries but not within the interior of the grains. Consequently, the surfaces of these alloys had external scales of  $\text{Cr}_2\text{O}_3$  over the grain boundaries but internal  $\text{Cr}_2\text{O}_3$  subscales with external scales of  $\text{NiO}$  away from the grain boundaries. Under these latter conditions, it was found that chromium could diffuse laterally in the alloy from those areas covered with an external layer of  $\text{Cr}_2\text{O}_3$ , i.e., grain boundaries, to areas where the  $\text{Cr}_2\text{O}_3$  was present as a subscale. This diffusion of chromium resulted in an increase in the volume fraction of  $\text{Cr}_2\text{O}_3$  precipitated in the subscale zone and continuous layers of  $\text{Cr}_2\text{O}_3$  could be formed at the subscale front in these regions. For the alloys used in the previous studies,<sup>1</sup> continuous layers of  $\text{Cr}_2\text{O}_3$  were formed on Ni-20Cr alloys in the subscale regions after approximately 30 hr of oxidation at 900°C. For shorter periods of oxidation, the  $\text{Cr}_2\text{O}_3$  layer was semicontinuous with the continuous portion at the subscale front emanating from points where the  $\text{Cr}_2\text{O}_3$  had been formed as an external scale over alloy

grain boundaries. Some lateral growth of a  $\text{Cr}_2\text{O}_3$  layer in the subscale region was observed on Ni-15Cr and even Ni-10Cr alloys but this layer was never continuous after 30 hr of oxidation.

These results indicate that the selective oxidation of chromium in Ni-Cr alloys with chromium contents between 5 to 30 pct may be dependent upon the grain size of the alloy. Fine-grained specimens in this compositional range should have a larger fraction of the surface covered with external  $\text{Cr}_2\text{O}_3$  than coarse-grained specimens and the subscale areas required to be sealed via lateral diffusion of chromium should be smaller. It is therefore to be expected that a continuous layer of  $\text{Cr}_2\text{O}_3$  can be formed on alloys in this compositional range after short periods of oxidation providing the alloy grain-size is sufficiently small.

Some studies<sup>3,4</sup> have established that the oxidation behavior of alloys can be significantly influenced by pretreatments which produce mechanically deformed surfaces. It has been found that deformed surfaces usually promote the selective oxidation of elements in alloys and it is believed that these effects are due to rapid diffusion of elements in the deformed metal. In view of the previous results,<sup>1</sup> which showed that alloy grain boundaries may play an important role in the selective oxidation of chromium in Ni-Cr alloys, deformed surfaces may promote the selective oxidation of elements in alloys as a result of the numerous grain boundaries formed on the alloy surfaces via recrystallization during heating to the oxidation temperature. The purpose of the present studies was to determine the effect of alloy grain size and surface deformation on the selective oxidation of chromium in Ni-Cr alloys at temperatures of 900° and 1100°C in 0.1 atm of oxygen.

## EXPERIMENTAL

The average grain diameter of the alloys used in the previous studies<sup>1</sup> was not less than 0.04 mm and alloys with compositions between 5 and 30 pct chromium had average grain diameters between 0.04 and 0.14 mm. Since the oxidation kinetics were already available for these relatively coarse-grained alloys, it was desirable to use these same alloys in the present studies. The surfaces of the alloys listed in Table I of the previous paper were deformed by using a Model F S.S. White Industrial Abrasive Unit, which delivered a controlled mixture of 25  $\mu$   $\text{Al}_2\text{O}_3$  particles in a stream of dry air at high velocity against the surface of a specimen. The amount of surface deformation produced by this treatment was not determined but a recrystallized layer about 15  $\mu$  thick was formed upon annealing deformed specimens.

The grain size at the surface of the specimens was reduced to an average grain diameter of 0.01 mm by annealing the deformed specimens, i.e., grit-blasted,

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for 2 hr at 900°C in vacuum. The structures of a typical specimen before and after the deformation-annealing treatment are compared in Fig. 1. The fine grains on the surface of grit-blasted-annealed specimens were very stable at 900°C and the grain diameter was virtually unchanged even after a 20-hr anneal at this temperature. At 1100°C grain growth was quite rapid and the average grain diameter eventually exceeded 0.01 mm. Consequently, stress-free, fine-grained specimens were tested at 900°C and alloys with deformed surface layers were tested at 900° and 1100°C.

The apparatus used in the oxidation experiments, experimental procedure, e.g., specimen size, cleaning of specimens, and so forth, and techniques used to examine oxidized specimens were the same as those described in the preceding paper.<sup>3</sup>

## RESULTS

**Weight-Change Measurements.** Typical curves obtained from weight-change vs time measurements for grit-blasted and grit-blasted-annealed specimens are

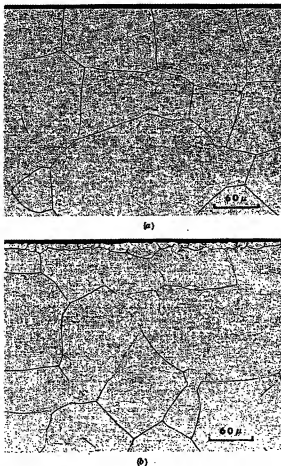


Fig. 1—Effect of surface pretreatment on a Ni-15Cr alloy heat treated for 2 hr in vacuum at 900°C. (a) Electropolished surface. (b) Grit-blasted surface. Etchant: 30 ml  $H_2PO_4$ , 170 ml  $H_2O$ . Electrolytic, Pt-Pt (2 v for ~30 sec).

presented in Figs. 2 and 3 for temperatures of 900° and 1100°C, respectively. The data for all specimens eventually followed a parabolic rate law although the oxidation kinetics frequently deviated from such a relationship during the early stages of oxidation. In Fig. 4 the parabolic rate constants obtained for grit-blasted and grit-blasted-annealed specimens are compared to the rate constants obtained for electropolished, coarse-grained samples. The results presented in this figure for experiments performed at 900°C show that the rate constants obtained for grit-blasted and grit-blasted-annealed specimens are similar but significantly less than the parabolic rate constants obtained for electropolished, coarse-grained specimens. At 1100°C the grit-blasted specimens oxidized at slower rates than specimens of the same composition in the stress-free, electropolished condition.

**Examination of Oxidized Specimens.** The microstructure of grit-blasted and grit-blasted-annealed specimens were identical after oxidation in 0.1 atm of oxygen at 900°C. Alloys with these surface preparations and containing 10 pct or more chromium, developed thin, external oxide scales during oxidation

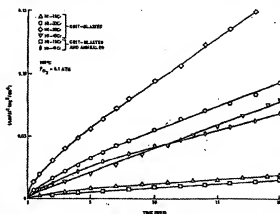


Fig. 2—Typical oxidation data for grit-blasted and grit-blasted-annealed Ni-Cr alloys at 900°C.

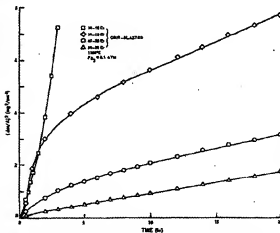


Fig. 3—Typical oxidation data for grit-blasted Ni-Cr alloys at 1100°C.

as shown in Fig. 5. X-ray diffraction analyses of these oxide scales showed that  $\text{Cr}_2\text{O}_3$  was the principal phase.  $\text{NiCr}_2\text{O}_4$  was also detected but the intensity of diffraction lines for this phase were quite weak indicating that it was probably formed during the initial stages of oxidation before a continuous layer of  $\text{Cr}_2\text{O}_3$  could be developed. The oxidation attack of alloys with grit-blasted or grit-blasted-annealed pretreatments was not uniform when the alloy contained less than 10 pct Cr and occasionally the oxidation rates of alloys in this compositional range were observed to increase with time as shown in Fig. 4. The microstructure of a typical specimen is presented in Fig. 6. Some portions of the surface are covered with a thin layer of  $\text{Cr}_2\text{O}_3$  while other portions have an external scale of  $\text{NiO}$  with a  $\text{Cr}_2\text{O}_3$  subscale. It is evident that the chromium was not selectively oxidized uniformly over the entire specimen surface. On the coarser grained alloys, i.e., electropolished specimens, external scales of  $\text{Cr}_2\text{O}_3$  were observed on specimens with 30 pct or more Cr while substantial amounts of  $\text{NiO}$  were found on alloys with smaller chromium contents. Specimens of electropolished and grit-blasted Ni-10Cr which were oxidized at  $900^\circ\text{C}$  are compared in Fig. 7. A thick, external scale of  $\text{NiO}$  with a subscale of  $\text{Cr}_2\text{O}_3$  has been formed on the electropolished specimen whereas a thin, external scale of  $\text{Cr}_2\text{O}_3$  is present on the grit-blasted specimen. In this photograph the  $\text{Cr}_2\text{O}_3$  is barely visible on the grit-blasted specimen but the zone of small grains at the specimen surface are easily discernible. The results obtained at  $900^\circ\text{C}$

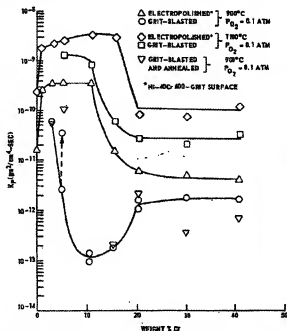


Fig. 4—Composition dependence of the parabolic rate constants for the oxidation of electropolished, 600-grit for Ni-40Cr, and grit-blasted nickel-chromium alloys at  $900^\circ\text{C}$  and  $1100^\circ\text{C}$ . Data for grit-blasted-annealed alloys oxidized at  $900^\circ\text{C}$  are also included. (The kinetic data for the grit-blasted Ni-Cr alloy exhibited two parabolic regions with the larger rate constant occurring at the later times.)

show that the chromium content above which continuous external scales of  $\text{Cr}_2\text{O}_3$  are formed on Ni-Cr alloys has been reduced from 30 to 10 pct by the grit-blasting or grit-blasting-annealing treatments.

At  $1100^\circ\text{C}$  thin, external oxide scales were formed on grit-blasted specimens during oxidation when the alloy contained 30 pct or more Cr. X-ray diffraction analysis of these oxide scales showed that  $\text{Cr}_2\text{O}_3$  was the principal phase in the scale. Trace amounts of  $\text{NiCr}_2\text{O}_4$  were also observed in the scale. Oxidized specimens of grit-blasted Ni-15Cr and Ni-15Cr alloys exhibited a continuous layer of  $\text{Cr}_2\text{O}_3$  on the alloy surface, however, at some areas the  $\text{Cr}_2\text{O}_3$  layer had formed beneath a layer of  $\text{NiO}$  as shown in Fig. 8(a). The Ni-20Cr specimens had fewer of these areas, i.e.,  $\text{Cr}_2\text{O}_3$  beneath  $\text{NiO}$ , than the Ni-15Cr samples. The oxidation attack of grit-blasted specimens containing less than 15 pct Cr was not uniform as shown in Fig. 9. It can be seen that on some areas of the alloy surface an external layer of  $\text{Cr}_2\text{O}_3$  has been formed while in other areas external scales of  $\text{NiO}$  with  $\text{Cr}_2\text{O}_3$  subscales

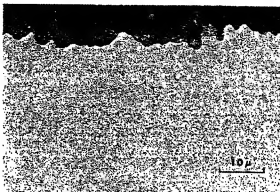


Fig. 5—Microstructure of a grit-blasted Ni-20Cr alloy after 65 hr of oxidation at  $900^\circ\text{C}$  in 0.1 atm of oxygen. An external scale of  $\text{Cr}_2\text{O}_3$  has been formed.

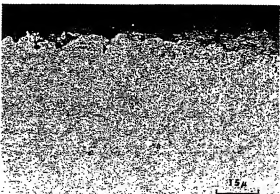


Fig. 6—Microstructure of a grit-blasted Ni-5Cr alloy after 19 hr of oxidation at  $900^\circ\text{C}$  in 0.1 atm of oxygen. The oxidation attack is not uniform. In some areas a thin external scale of  $\text{Cr}_2\text{O}_3$  is visible while in other areas  $\text{NiO}$  with  $\text{Cr}_2\text{O}_3$  subscales are evident.

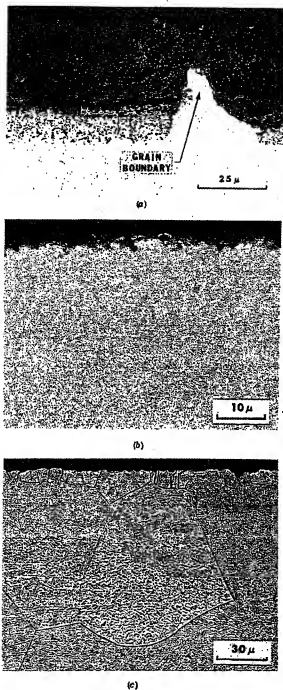


Fig. 7—Effect of surface pretreatment on a Ni-10Cr alloy oxidized for 20 hr in 0.1 atm of oxygen at 900°C. (a) Electropolished surface. A two-zoned layer of NiO and a  $\text{Cr}_2\text{O}_3$  subscale has been formed. Some lateral growth of the  $\text{Cr}_2\text{O}_3$  scale is evident at a grain boundary. (b) Grit-blasted surface. An external scale of  $\text{Cr}_2\text{O}_3$  which is barely discernible has been formed. (c) Specimen described in (b) in etched condition. Note the small grains which were formed by recrystallization of the deformed surface layer. Etchant: Aged solution of 30 ml Lactic acid, 20 ml Acetic acid, 30 ml HCl, 10 ml  $\text{HNO}_3$ , Immersion.

are evident. The microstructure of oxidized, electropolished, coarse-grained specimens was identical to that of grit-blasted samples when the alloy contained 30 pct or more Cr. In the case of the oxidation of electropolished specimens, containing less than 30 pct Cr, external scales of NiO with  $\text{Cr}_2\text{O}_3$  subscales were formed. In the  $\text{Cr}_2\text{O}_3$  subscale zone, a continuous layer of  $\text{Cr}_2\text{O}_3$  was observed on the Ni-20Cr alloy after approximately 30 hr of oxidation but no continuous  $\text{Cr}_2\text{O}_3$  layer was observed on alloys with smaller chromium contents. In Figs. 8(a) and (b) oxidized specimens of a grit-blasted and an electropolished Ni-15Cr alloy are compared. The grit-blasted specimen has a continuous layer of  $\text{Cr}_2\text{O}_3$ , whereas a  $\text{Cr}_2\text{O}_3$  subscale has been formed on the electropolished specimen. The results obtained at 1100°C also show that the selective oxidation of chromium has been promoted by the grit-blasting treatment.

**Experiments Using  $\text{CO-CO}_2$  Gas Mixtures.** To examine the behavior of a Ni-Cr alloy with different surface preparations, under conditions where NiO

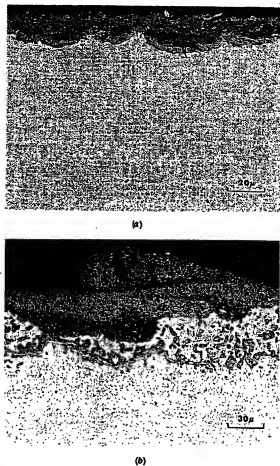


Fig. 8—Comparison of the oxide scales formed on grit-blasted and electropolished specimens of Ni-15Cr alloy after oxidation at 1100°C in 0.1 atm of oxygen. (a) Grit-blasted surface. A continuous layer of  $\text{Cr}_2\text{O}_3$  has formed beneath a layer of NiO. (b) Electropolished surface. The chromium has been oxidized internally and appears as a subscale beneath the NiO layer.

was not stable, a Ni-10Cr alloy with an average grain diameter of about 0.1 mm was electropolished and then one-half of the surface was grit-blasted. This specimen was then oxidized in a CO-CO<sub>2</sub> mixture with CO/CO<sub>2</sub> = 0.07 at 900°C. The surface of this oxidized specimen is shown in Fig. 10(a) which shows that an external scale of Cr<sub>2</sub>O<sub>3</sub> has been formed on the grit-blasted portion of the surface while on the coarse-grained, electropolished area Cr<sub>2</sub>O<sub>3</sub> has been formed only at grain boundaries. A cross-sectional view of this specimen is presented in Fig. 10(b). It is evident that the chromium has been oxidized externally over the grit-blasted area but internally over the electropolished surface. Similar results were obtained when such a specimen was annealed in vacuum after the grit-blasting treatment prior to the oxidation reaction.

#### DISCUSSION OF RESULTS

The results obtained with grit-blasted and grit-blasted-annealed specimens at 900°C were similar. The annealed alloys were known to have a thin layer of fine, stress-free grains on their surfaces during the entire period of oxidation and the grit-blasted alloys were found to have similar structures when examined after oxidation. It therefore appears that the deformation introduced during the grit-blasting treatment affects the oxidation behavior of Ni-Cr alloys by producing numerous grain boundaries on the alloy surface via the recrystallization which occurs as the specimen is heated to the test temperature.

The results presented in Fig. 4 show that at both 900°C and 1100°C the oxidation rates of all Ni-Cr alloys with fine grains, i.e., grit-blasted or grit-blasted-annealed, are smaller than the oxidation rates of alloys with the same composition but which have coarser grains at their surfaces, i.e., electropolished. However, the microstructure of oxidized specimens was found to be dependent upon the alloy grain size only when the alloy contained less than 30 pct Cr, see Figs. 7 and 8. In view of this condition it is convenient to discuss the behavior of alloys containing less than 30 pct Cr first and then proceed to the alloys with larger chromium concentrations.



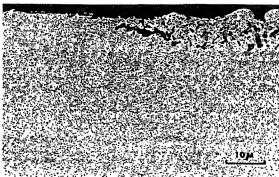
Fig. 9—Microstructure of a grit-blasted Ni-10Cr alloy after 20 hr of oxidation at 1100°C in 0.1 atm of oxygen. The oxidation attack is not uniform. In some areas a thin external scale of Cr<sub>2</sub>O<sub>3</sub> is visible while in other areas clumps of NiO with Cr<sub>2</sub>O<sub>3</sub> subscales are evident.

**Alloys With Less than 30 pct Cr.** The results obtained in the present studies show that continuous, external scales of Cr<sub>2</sub>O<sub>3</sub> are formed on the fine-grained Ni-Cr alloys at lower chromium concentrations than on the coarse-grained alloys. This difference in behavior is believed to result from the larger number of grain boundaries that are present on the surfaces of the fine-grained alloys. During the early stages of oxidation of a Ni-Cr alloy with less than 30 pct Cr, chromium is oxidized externally at alloy grain boundaries but internally at other areas on the alloy surface. When the alloy has a small grain size, i.e., ≈0.01 mm, the Cr<sub>2</sub>O<sub>3</sub> in the subscale region becomes continuous as a result of the lateral diffusion of chromium to the subscale front from those areas where Cr<sub>2</sub>O<sub>3</sub> exists as a continuous layer. As the alloy grain size is increased the chromium content of the alloy must also be increased before a continuous layer of Cr<sub>2</sub>O<sub>3</sub> will be formed in the subscale region since the larger diffusion distances result in a smaller increase in the volume fraction of precipitated Cr<sub>2</sub>O<sub>3</sub> due to lateral diffusion of chromium.

The smaller oxidation rates of fine-grained alloys compared to those for coarse-grained alloys are a result of the increased selective oxidation of chromium



(a)



(b)

Fig. 10—Effect of surface pretreatment on a Ni-10Cr alloy oxidized for 20 hr in a CO-CO<sub>2</sub> mixture (CO/CO<sub>2</sub> = 0.07) at 900°C. Prior to oxidation one-half of the surface was electropolished and the other half was grit-blasted. Chromium has been oxidized externally on the grit-blasted surface but internally in the electropolished area except at alloy grain boundaries where it has also been oxidized externally.  
(a) Surface topography. (b) Transverse section.



for fine-grained alloys. External scales of  $\text{Cr}_2\text{O}_3$  are formed on fine-grained alloys during oxidation while substantial amounts of  $\text{NiO}$  are formed on the surfaces of coarse-grained alloys with the same bulk composition. Since transport through  $\text{Cr}_2\text{O}_3$  is slower than transport through  $\text{NiO}$ , the fine-grained alloys therefore have smaller oxidation rates than the coarse-grained alloys. Examination of Fig. 4 shows that the parabolic rate constants for fine-grained alloys are dependent upon the chromium content of the alloy. Below 10 pct Cr at  $900^\circ\text{C}$  and below 20 pct Cr at  $1100^\circ\text{C}$  the oxidation rates of fine-grained alloys begin to increase and have poor reproducibility because continuous external  $\text{Cr}_2\text{O}_3$  scales are not formed over the entire surface and  $\text{NiO}$  is formed in some areas as shown in Figs. 6 and 9. Smaller chromium contents are sufficient for selective oxidation at  $900^\circ\text{C}$  because smaller grains are formed in the recrystallized layers than at  $1100^\circ\text{C}$ . The oxidation rates of these alloys are still smaller than those of coarse-grained alloys with similar compositions since uniform external scales of  $\text{NiO}$  and  $\text{Cr}_2\text{O}_3$  subscales are formed on coarse-grained alloys. The nonuniform oxidation of fine-grained alloys is believed to result from local variations in the grain size on the surfaces of the alloys which indicates that continuous, external scales of  $\text{Cr}_2\text{O}_3$  may form on alloys with lower chromium concentrations than those determined in the present studies providing the alloy grain size can be made smaller than that of the fine-grained alloys used in the present experiments.

At  $900^\circ\text{C}$  the parabolic rate constants for fine-grained alloys increase with alloy chromium content from 10 to 20 pct Cr and are constant for larger chromium concentrations. The dependence of the parabolic rate constants on the chromium content of the alloy when  $\text{Cr}_2\text{O}_3$  is the only oxide formed upon the alloy surface has been discussed in the preceding paper.<sup>1</sup> It can be shown that the parabolic rate constants for fine-grained alloys at  $900^\circ\text{C}$  should increase with chromium content up to about 19 pct Cr and then become constant. The data in Fig. 4 for  $900^\circ\text{C}$  are consistent with these considerations. A similar effect is not observed at  $1100^\circ\text{C}$  because even though a continuous layer of  $\text{Cr}_2\text{O}_3$  has been found on alloys with 15 and 20 pct Cr, substantial amounts of  $\text{NiO}$  were formed before the  $\text{Cr}_2\text{O}_3$  scale became continuous, see Fig. 8. The formation of  $\text{NiO}$  results in an abrupt increase of the weight-gain vs time curves during the early stages of oxidation which causes the parabolic rate constants calculated from these data to be larger than those for the growth of  $\text{Cr}_2\text{O}_3$ .

Alloys With Greater than 30 pct Cr. At both temperatures the parabolic rate constants for alloys containing 30 pct or more Cr are independent of the bulk chromium content of the alloy. This is to be expected for the growth of  $\text{Cr}_2\text{O}_3$  scales on alloys with large chromium concentrations. At both temperatures the parabolic rate constants of fine-grained specimens

are smaller than those of coarse-grained samples. In the case of alloys with these chromium contents, both fine and coarse-grained specimens formed external layers of  $\text{Cr}_2\text{O}_3$  virtually at the onset of oxidation. The rate constants for fine-grained or deformed specimens were about a factor of three smaller than those for electropolished specimens which were oxidized under similar conditions. This difference is not large; however, since these fine-grained or grit-blasted specimens were always observed to oxidize slower than electropolished specimens, it is believed to be a true effect. Factors such as modification of the oxide scale on account of the electropolishing treatment,<sup>1</sup> surface area changes and contamination of the surfaces of grit-blasted specimens with the abrasive material were found to have negligible effects on the parabolic rate constants of these alloys. The results can be explained if one assumes that short circuit diffusion paths are present in the  $\text{Cr}_2\text{O}_3$  formed on the electropolished specimens or that void formation occurs at the  $\text{Cr}_2\text{O}_3$ -alloy interface on grit-blasted specimens. However, such assumptions are speculation at this time and an explanation for the decreased parabolic rate constants for grit-blasted or fine-grained alloys which contained 30 pct or more Cr is not available.

#### SUMMARY AND CONCLUDING REMARKS

The oxidation properties of Ni-Cr alloys with fine grains, coarse grains, and deformed surface layers have been compared. The behavior of alloys with fine grains and with deformed surface layers has been found to be the same and it has been concluded that deformed surfaces affect the oxidation properties of Ni-Cr alloys at temperatures of  $900^\circ$  and  $1100^\circ\text{C}$  by producing fine grains via recrystallization of the cold worked layer as the specimen is heated to the oxidation temperature. The oxidation properties of Ni-Cr alloys with chromium concentrations between 10 and 30 pct have been found to be dependent upon the grain size of the alloy. This effect is caused by the selective oxidation of chromium at alloy grain boundaries over this compositional range.

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## THE EFFECT OF SURFACE PREPARATION ON THE OXIDATION BEHAVIOR OF GAMMA TiAl-BASE INTERMETALLIC ALLOYS

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### Introduction

Titanium aluminides, specifically the intermetallic compound gamma TiAl, are being investigated as potential aerospace and automotive materials due to high specific strength and stiffness (1-6). The oxidation behavior of gamma TiAl has been studied extensively (7-22). Oxygen exposures tend to produce slow growing alumina rich scales at low temperatures. At higher temperatures (approximately 800°C), the alumina breaks down locally and mixed oxide nodules form. At temperatures at and above 1000°C, the nodules grow rapidly and merge to form a thick mixed oxide scale. The oxidation behavior in atmospheres containing nitrogen is significantly different. Nitrogen reacts with titanium in the alloy to form titanium nitrides at the scale/alloy interface. The result is a discontinuous layer of aluminum oxide particles at the scale/alloy interface. It is not possible to form a continuous, protective alumina layer, resulting in rapid oxidation in air. Important initial research also pointed to surface preparation as a potential factor in the oxidation behavior of gamma TiAl alloys (23).

The material used for this study was stoichiometric Ti-50Al (nominal composition in atomic percent), a single phase  $\gamma$  TiAl alloy with large equiaxed grains. In addition, material with a lower aluminum content (Ti-48Al) was also investigated. This alloy is notable because it contains significant amounts of the intermetallic alpha-2 Ti<sub>3</sub>Al dispersed in small lamellar colonies as a second phase.

### Experimental Procedure

Oxidation specimens were prepared by cutting on a low speed diamond saw and then grinding through 600 grit SiC paper. Thermogravimetric analysis (TGA) was used to record continuous mass change as a function of time at elevated temperatures during exposure to a controlled atmosphere. Selected specimens were then polished with 1 micron diamond paste. X-ray diffraction analysis of oxide scales was performed with a Philips diffractometer in both normal and glancing angle ( $1^\circ$ ) modes. Morphological

analysis was carried out on a JEOL 35CF SEM equipped with EDS and WDS. A face-to-face mounting technique was employed to fabricate cross-section TEM specimens, which were thinned to electron transparency by dimpling and subsequent ion milling on a Gatan PIPS mill at a 4° angle of incidence. Transmission electron microscopy was performed primarily on a JEOL 2000FX equipped with a light element EDS system.

### Results and Discussion

#### 600 Grit Surface Finish

Exposure to oxygen results in small weight gains due to oxygen uptake at temperatures lower than 800°C for specimens prepared to 600 grit. The scale which forms is rich in alumina and transport through it is slow. The weight gain increases at 900°C due to the formation of mixed oxide nodules, which are locally thicker regions of the scale consisting of a mixture of rutile  $\text{TiO}_2$  and alumina (Fig. 1). Transport across the scale is more rapid due to the partition of cross-sectional areas into regions of slow transport through alumina and rapid transport through nodules, as can be noted from surface scanning electron micrographs (Fig. 2). A set of short time exposures in oxygen proved that nodules form specifically at sites of alpha-2 in the microstructure for exposures of the Ti-48Al alloy (Fig. 3). After thirty minutes, the alpha-2 lamellae are decorated with thick oxide, while the surrounding gamma grains form a thin alumina film. A two hour exposure results in the formation of nodules at the lamellae sites. After five hours, the lamellar regions are completely consumed by mixed oxide nodules, which cease to grow past the boundaries of the alpha-2 colonies, as verified by 180 and 360 hour experiments. At 1000°C the weight gain increases by an order of magnitude due to sudden rapid growth and merging of nodules (Fig. 4). A thick mixed scale forms and diffusion through rutile  $\text{TiO}_2$  is dominant. It is not known why the nodules suddenly break free. It is possible that the ternary oxide  $\text{TiAl}_2\text{O}_3$  forms, but the equilibrium transformation temperature for the reaction between  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  is 1100°C (24). Exposure to air at high temperatures results in larger mass gains at all temperatures when compared to corresponding oxygen exposures, as can be noted from the oxidation kinetics (Fig. 5). The scale forms in a homogeneous manner, and the final product is similar to the scale formed at 1000°C in oxygen. This is caused by the formation of titanium nitrides at the scale/alloy interface, which oxidize to titanium oxide and prevent the scale from becoming continuous (25-26).

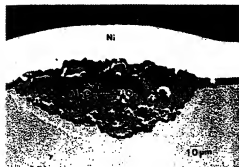


Figure 1. Cross-section SEM micrograph, Ti-50Al, 600 grit surface finish, 1 week, 900°C, oxygen.



Figure 2. Surface SEM micrograph, Ti-50Al, 600 grit surface finish, 1 week, 900°C, oxygen.

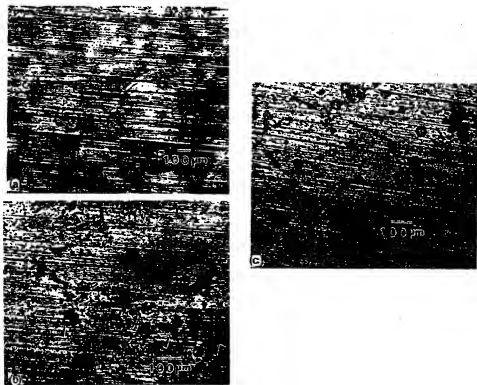


Figure 3. Surface optical micrographs, Ti-48Al, 600 grit surface finish, 900°C, oxygen. a) 30 minutes; b) 2 hours; c) 5 hours.

### 1 Micron Surface Finish

Specimens polished to 1  $\mu\text{m}$  exhibit accelerated oxidation in pure oxygen with respect to specimens finished to 600 grit. The weight gain of the 1  $\mu\text{m}$  finished specimen is comparable an air exposure at the same temperature (Fig. 5). A thick mixed-scale forms, rather than a typical alumina film broken sporadically by mixed oxide nodules. Variations in surface finish were found to have no effect in an air atmosphere. The parabolic rate constants as well as the activation energy obtained by plotting these constants versus  $1/T$  for the air exposures, 1  $\mu\text{m}$  surface finish oxygen exposures, and 1000°C 600 grit surface finish oxygen exposures all are similar to that for diffusion in rutile  $\text{TiO}_2$ . The consistent reduction in the parabolic rate constant compared to a perfect rutile former is due to the formation of alumina in the scale, which reduces the effective rutile diffusion cross-sectional area. This increases the diffusion distance and reduces the oxidation rate somewhat. Lower temperature 600 grit oxygen exposures result in oxidation kinetics approaching those for alumina growth.

Oxidized specimens with both 600 grit and 1  $\mu\text{m}$  surface finishes were examined in cross-section with transmission electron microscopy. Both specimens formed a titanium-rich phase with a lattice parameter of 6.9Å and cubic symmetry. The diffraction patterns from this phase do not match any relevant phases known for the Ti-Al-O-N system. Dowling and Donlon first reported the existence of this phase and the lattice parameter (27). Zheng et al. have recently published X-ray diffraction data which is consistent with the work of Dowling and Donlon (28). Convergent beam electron diffraction analysis reveal a cubic phase with either the P432 or P4<sub>3</sub>2 space group (29). The major difference

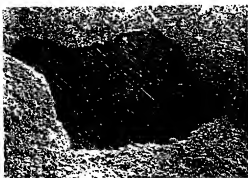


Figure 4. Surface SEM micrograph, Ti-50Al, 1 week, 1000°C, oxygen.

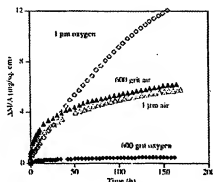


Figure 5. TGA data for Ti-50Al; air and oxygen exposures, 600 grit and 1  $\mu$ m specimens, 900°C.

between the two specimens is that the one with a 600 grit surface finish exhibits a recrystallized gamma TiAl zone within the alloy, which formed during the early stages of oxidation (less than 1 hour) (Fig. 6). Specimens with a 1 micron finish do not exhibit this recrystallized gamma layer (Fig. 7). Similar effects have been observed in the nickel-chromium system by Giggins and Pettit (30). Compared to the unexposed alloy, which has an approximate grain size of 100 microns, the grain size of the recrystallized grains is quite small. The introduction of this layer increases the grain boundary area near the specimen surface by a large amount.

### Conclusions

Parabolic rate constant analysis confirms that rapid oxidation of gamma TiAl corresponds to rutile  $\text{TiO}_2$  formation. It is established that air exposures result in the nitrogen effect, causing titanium nitride formation and subsequent rutile-dominated oxidation kinetics. When rutile forming kinetics dominate, the system is close to a maximum rate of oxidation. Therefore, surface finish is irrelevant in air, as the effect cannot drive the system to oxidize any faster. In oxygen, the rate is between that for alumina and rutile formation for abraded surfaces, indicating a primarily alumina scale. With a finely polished surface or very high temperatures, the oxidation rate increases several orders of magnitude, corresponding to mainly rutile formation. Once again, the material has reached a maximum oxidation rate for the temperature considered. Recent work by Becker, et al., reports a higher oxidation rate in oxygen compared to air at 900°C, with the opposite occurring at 1000°C (7). This inconsistent result can be explained by noting that the samples investigated were polished with 4000 grit SiC paper, which is significantly finer than the 600 grit paper used in this study and others. At 900°C, the effect of surface finish leads to more rapid oxidation in oxygen. At 1000°C, the effect of surface finish is masked by overall rapid oxidation due to nodule growth.

The variation of oxidation behavior of gamma TiAl in oxygen seems to be a direct consequence of the formation of a recrystallized zone within the alloy as a result of energy stored by near-surface deformation induced by the grinding process. The recrystallization promotes the formation of an alumina film in oxygen. Such an effect is not unknown in other alloy systems. Giggins and Pettit observed a similar phenomenon in the Ni-Cr system (30). The gamma alloys studied possess coarse grain size. Recrystallization results in the addition of many grain boundaries. It is likely that this layer is enhancing diffusion via short circuits within the alloy, increasing the diffusivity of species to the scale/alloy interface. Increasing the aluminum diffusivity in the alloy would result in stability of aluminum oxide

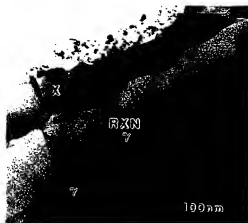


Figure 6. XTEM micrograph, Ti-50Al, 1 hour, 900°C, oxygen, 600 grit surface finish.



Figure 7. XTEM micrograph, Ti-50Al, 1 hour, 900°C, oxygen, 1 μm surface finish.

at lower aluminum content by reducing aluminum depletion/titanium enrichment. Another possibility is that the high dislocation density at the surface of the abraded specimen may provide another short circuit path. However, the recrystallized layer forms within five minutes, so dislocations would only play a role in the earliest stage of oxidation before they are eliminated by recrystallization.

The surface finish effect does not exist in air. A different oxidation mechanism is operative, with the nitrogen effect precluding the formation of an alumina layer. Enhanced substrate diffusion plays little or no role in increasing the oxidation resistance. However, recent research has indicated that at lower temperatures (600°C), TiAl alloys no longer react with nitrogen (31). The surface finish may then play a role in both air and oxygen atmospheres.

In the future, work in this area will concentrate on examination of both unexposed and very short time exposure cross-sections. Examination of the near-surface regions of unexposed specimens will serve to characterize the induced deformation with respect to bulk material before any transformation due to oxidation occurs. The very short time exposures are needed to characterize the initial stages of recrystallization, i.e. nucleation sites and reaction kinetics.

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